

## Application Note

# Determination of the Bromine Index of Petroleum Hydrocarbons Using Electrometric Titration

Industry	:	Chemicals
Instrument	:	Automatic potentiometric titrator
Measurement method	:	Constant voltage polarization titration
Standards	:	ASTM D 2710

## 1. Scope

The bromine index indicates the amount of a component with unsaturated bonds. It is defined as the number of mg of bromine that reacts with 100 g of a sample. In ASTM D 2710, measurement of the bromine index is stipulated as an index of the amount of an unsaturated trace compound in a petroleum fraction at 288 °C (550 °F) or lower. In these standards, only samples that satisfy all of the following conditions can be used.

- The bromine index is under 1,000.
- The sample does not contain a substance less dense than isobutane.
- Petroleum fraction at 288 °C (550 °F) or lower
- The main component must be olefin-free hydrocarbons or mixtures.

In the example in this Application Note, a sample solution of cyclohexene dissolved in isooctane is measured in accordance with ASTM D 2710.

## 2. Apparatus

Main unit	:	Automatic potentiometric titrator (polarization titration preamplifier :POT)
Electrode	:	Twin platinum electrode, Temperature compensation electrode

## 3. Reagents

Titrant	:	0.05 mol/L Bromide-Bromate Standard Solution (potassium bromide and potassium bromate)
Titration solvent	:	Solution consisting of a mixture of 714 mL of acetic acid, 134 mL of 1,1,1-trichloromethane or dichloromethane, 134 mL of methanol, and 18 mL of sulfuric acid (1 + 5)

## 4. Procedure

### -Calibration-

- 1) Place approximately 8 g of the sample in a beaker and add 110 mL of titration solvent.
- 2) While stirring, cool the sample in an ice bath until the temperature reaches 5 °C or lower.
- 3) Set the voltage applied to the twin platinum electrodes to 300 mV.
- 4) Immerse the twin platinum electrodes in the sample solution and calibrate.

### -Blank test-

- 1) Add 110 mL of titration solvent to a beaker.
- 2) While stirring, cool the sample in an ice bath until the temperature reaches 5 °C or lower.
- 3) Titrate with 0.025 mol/L of bromine solution.

### -Measurement-

- 1) Weigh out precisely 8 g of the sample and place it in a beaker.
- 2) Add 110 mL of titration solvent to the beaker.

- 3) While stirring, cool the sample in an ice bath until the temperature reaches 5 °C or lower.
- 4) Titrate with 0.025 mol/L of bromine solution.

## 5. Calculation

$$\text{Bromine index (mgBr}_2\text{/100g)} = (\text{EP1} - \text{BL1}) \times \text{TF} \times 0.05 \times 7990 / \text{S}$$

EP1	:	Titration amount (mL)
BL1	:	Titration amount (mL) of Blank test = 0.0645(mL)
TF	:	Factor of Titrant = 1.0265
S	:	Sample size (g)

## 6. Example

### — Parameter —

<Titr. Mode> : Intermittent

<Titr. Form> : EP Stop

<Titr. Para.>

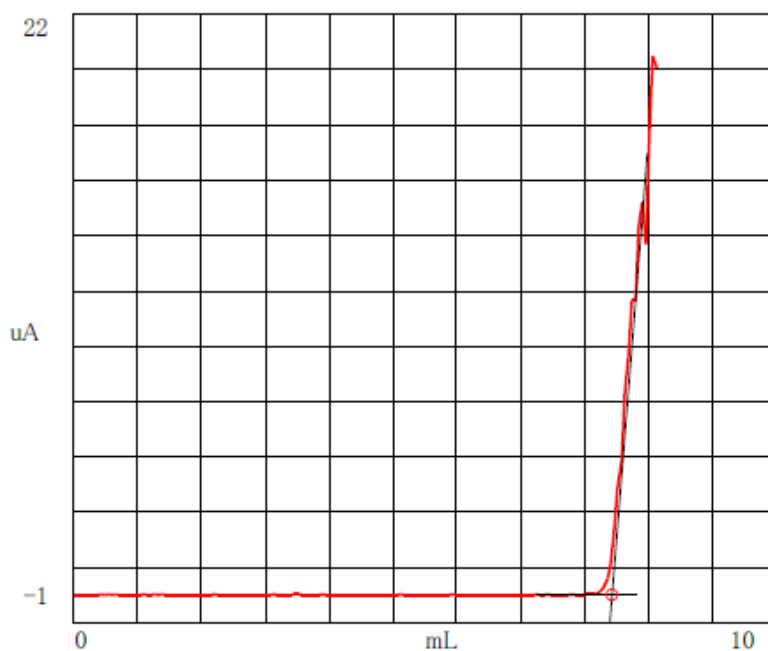
Max Volume : 20 (mL), Sample  
 Channel/Unit(Ctrl.) : Ch3,  $\mu\text{A}$   
 Wait Time : 0 (s)  
 Dose Mode : None

<Ctrl. Para.>

End Point No. : 1  
 End Sense (dE/dmL) : Auto  
 Gain : 1  
 Data sampling : Set  
 Data Samp. Pot. : 999mV  
 Data Samp. Vol. : 0.05mV  
 Ctrl. Speed : Set  
 Cut off time : 10s  
 Unit Volume : 0.05mL  
 Disp. Speed : 1s/mL  
 Cut off time : 10s  
 Other Control : Standard  
 Stirrer Speed : 4

(The settings above are just one example. They may vary depending on the model.)

### — Example of Titration curve —



## — Measurement results —

Table 1 Measurement result

	Sample (g)	Titration (mL)	Bromine index (mgBr <sub>2</sub> /100g)
1	8.1746	7.6665	381.4
2	8.1535	7.6065	379.3
3	8.3814	7.8517	381.0
Mean	-	-	380.6
SD	-	-	1.1
RSD (%)	-	-	0.3

## 7. Summary

The repeatability RSD was less than 1 %, showing that excellent accuracy can be achieved.

In ASTM D 2710, constant voltage polarization titration is stipulated as the measurement method. In this measurement method, a constant voltage is applied between the twin platinum electrodes, and the change in current as titration progresses is monitored.

Before the end point, the bromine is consumed through addition to the unsaturated bonds, so there is essentially no flow of current and a constant current value is shown. When the titration reaction is complete, if there is even a slight amount of excess bromine, a current will flow in the twin platinum cathode due to bromine reduction, and a sharp increase in the current value will be observed. The higher the bromine concentration, the longer the increase in the current value continues, so no inflection point appears in the titration curve. In this Application Note, automatic intersection detection was used as the end point detection method. This function automatically detects the end point at the intersection of two tangent lines drawn at the bend of the titration curve. If the end point cannot be detected automatically, there is also a function that uses the intersection of two manually drawn tangent lines as the end point.

KEM's titrators allow users to perform measurements in accordance with ASTM D 2710.

## 8. Reference

ASTM D 2710 Standard Test Method for Bromine Index of Petroleum Hydrocarbons by Electrometric Titration.