Application Note

Bromine number of olefines

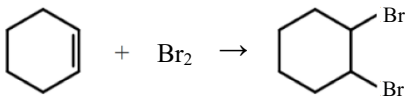
Industry	Petroleum
Instrument	Automatic potentiometric titrator
Measurement method	Potentiometric titration / Redox titration
Standard	UOP Method 304

1. Scope

The bromine number indicates the amount of a component with unsaturated bonds. It is defined as the number of grams of bromine consumed by 100g of sample (see Note 1). In this application note, bromine number is measured by potentiometric titration.

In this titration, the reaction is shown in equations (1) and (2). The bromine (shown in equation (1)) adds to carbon-carbon double bond. The equivalence point is defined as the point on the titration curve at which inflection occurs.

$$5KBr + KBrO_3 + 3H_2SO_4 \rightarrow 3Br_2 + 3K_2SO_4 + 3H_2O \quad \dots (1)$$



… (2)

Note 1 In this measurement, cyclohexene was dissolved in toluene and used as the sample.

2. Precaution

Prior to the first titration, prepare the burette by dispensing and aspirating the titrant between it and the reagent bottle several times. Once done, purge approximately 10mL of the titrant from the burette and out of the titration nozzle.

3. Apparatus

Main unit	Automatic potentiometric titrator (Preamplifier STD)
Electrode	Platinum electrode
	Double junction sleeve reference electrode
	(Inner filling：3.3mol/L potassium chloride solution)

4. Reagents

Titrant	0.25 mol/L potassium bromide - potassium bromate standard solution
Titration solvent	Mixture of 714 mL of glacial acetic acid, 134 mL of dichloromethane, 116 mL of methanol, 18 mL of 3 mol/L sulfuric acid, and 18mL of 10 % mercury(II) chloride methanolic solution.

5. Procedures

Blank titration

1) Transfer 100 mL of titration solvent into a beaker.
2) Wait for stabilization the potential in the range of -1000 to 1000 mV when the electrode is immersed in the titration solvent.
3) Titrate with 0.25 mol/L potassium bromide - potassium bromate standard solution.

Sample titration

1) Collect the sample into a beaker and measure the mass.
   - Collect the amount specified in UOP Method 304 corresponding to the bromine number of the sample. If the bromine number of the sample is over 24 $gBr_2/100g$, the sample should be collected after dilution to ensure the accuracy of the sampling volume. (See Note 2 and 3)
2) Transfer 100 mL of titration solvent to that beaker, and dissolve the sample completely.
3) Wait for stabilization the potential in the range of -1000 to 1000 mV when the electrode is immersed in the titration solvent.
4) Titrate with 0.25 mol/L Potassium bromide - potassium bromate standard solution.

Table 1. Sample size

Bromine number ($gBr_2/100g$)	Sample size (g)
0.8～3	4
3～6	2
6～12	1
12～24	0.5
24～120	0.1 (see Note 2)
120～240	0.05 (see Note 3)

Note 2 Take 1g of sample, dilute with dichloromethane to the marked line in a 50 mL measuring flask, and then collect 5mL.

Note 3 Take 0.5g of sample, dilute with dichloromethane to the marked line in a 50 mL measuring flask, and then collect 5mL.

6. Calculation

$$\text{Bromine number } (gBr_2/100g) = 15.9808 \times (EP1 - BL1) \times 0.25 \times TF / S$$

EP1	Titration amount of sample titration (mL)
BL1	Titration amount of blank titration (mL)
TF	Factor of titrant (1.012)
S	Quantity of sample (g)

7. Example

—Parameter—

〈Titr. Mode〉	Auto Int.	〈Ctrl. Para.〉	
〈Titr. Form〉	EP Stop	Number of EP	1
〈Titr. Para.〉		End Sense	Auto
Channel / Unit (Ctrl.)	Ch1, mV	Gain	1
Wait Time	0(s)	Data Sampling	Auto
Dose Mode	None	Ctrl. Speed Mode	Standard
Max. Volume (mL)	20(sample) 0.15(blank)	Other Control	Standard
		Auto Int. Mode	Standard (sample) Blank(blank)

(Listed above example settings. Availability of settings may vary by instrument model.)

—Example of titration curve—

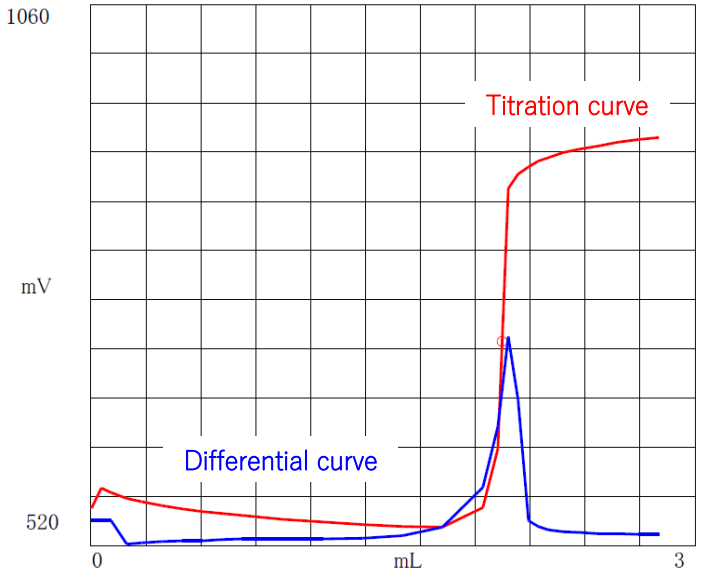


Table 2. Blank test

	Titration (mL)
1	0.0067
2	0.0072
3	0.0070
Mean	0.0070

Table 3. Sample 1 measurement result

	Sample (g)	Titration (mL)	Bromine number (gBr_2/100g)
1	4.0436	2.0457	2.04
2	4.0188	1.9965	2.00
3	4.0189	1.9776	1.98
Mean	-	-	2.01
SD	-	-	0.03
RSD (%)	-	-	1.5

Table 4. Sample 2 measurement result

	Sample (g)	Titration (mL)	Bromine number (gBr_2/100g)
1	1.2096	3.4762	11.59
2	1.0578	3.0454	11.61
3	1.0244	2.9122	11.46
Mean	-	-	11.55
SD	-	-	0.08
RSD (%)	-	-	0.7

8. Reference

UOP Method 304　BROMINE NUMBER AND BROMINE INDEX OF HYDROCARBONS BY POTENTIOMETRIC TITRATION