

AQUACOUNTER Application Sheet	COM series	DATA No. L9	1st edition
Petroleum Products		Measurement of bromine value in nonene	

1. Measurement outline

Measurement of bromine value for petroleum products (olefins, propylene, butane, nonene, etc.) is stipulated in JIS K 2605 as the evaluation test for products. Measurement of bromine value is an index that indicates the concentration of unsaturated bond components (compounds with double or triple bonds) contained in petroleum products, and it is expressed as the “g value of bromine consumed for 100g of sample.” Furthermore, besides the bromine value measurement for olefins stipulated in JIS K 2605, JIS K 2435 is also stipulated for the measurement of bromine value and bromine index of benzene, toluene, xylene, etc., and it shall be used for reference.

This section introduces an example in which the bromine value of nonene (theoretical bromine value 126) was measured according to JIS K 2605 using constant-current potentiometric titration method as the end point detection method instead of dead stop method (constant-voltage amperometric titration method).

In this measurement, approximately 20mL carbon tetrachloride is added in a 50mL graduated cylinder, into which approximately 2g is added using a glass syringe. The amount of sample to be added is calculated from the weight difference for the graduated cylinder before and after sample addition. Then carbon tetrachloride is added to the mark on the graduated cylinder and is mixed well. 5mL sample solution is collected using a whole pipette and added into 100mL titration solvent for titration with 5/60mol/L (0.5N) potassium bromide – potassium bromate titrant while cooling at approximately 5°C.



2. Reagents and Electrodes

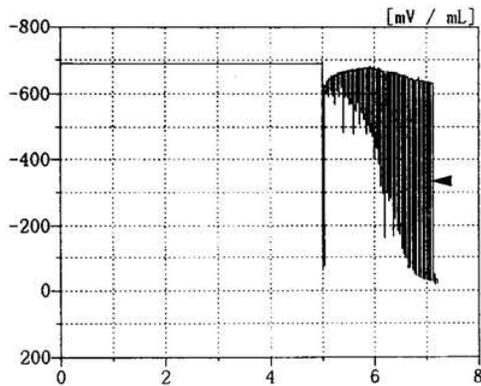
(1) Reagents	Titrant	5/60mol/L (0.5N) potassium bromide – potassium bromate titrant
	Titration solvent	Acetic acid 714mL Carbon tetrachloride 134mL Methanol 134mL Sulfuric acid (1+5) 18mL } 1L...110mL used for 1 measurement
(2) Electrodes	Twin Platinum electrode TPT-351 (P/N D231246-A) *P-2000 standard accessory	
	Polarization current 1 μ A	

3. Measurement conditions example (for COM-1600P w/ Polarization titration unit)

Master File No.1	
Condition file: 1	
Parameters for Condition file 1	
Method	AUTO
Buret No.	1
Meas Unit	mV
S-Timer	0 sec
CP mL	5 mL
DP mL	0 mL
Direction	N/A
End Sens	1000
Over mL	0.10 mL
Max Vol	20 mL
Mode No.	22
Unit	BN
Formula	$(D-B) \times F - M \times 7.99/S$
Blank	0
Molarity	0.5
Factor	Titre of the titrant
K	0

Mode No.22	
Pre Int	5 sec
Del K	0
Del Sens	0 mV
Int Time	5 sec
Int Sens	20 mV
Brst Speed	2
Pulse	32

4. Measurement example



Measurement results on bromine value for nonene

Sample No.	Sample volume (mL)	Titration value (mL)	Bromine value
1	0.2184	7.021	126.6
2	"	7.100	128.1
3	"	7.021	126.6
4	"	7.100	128.1
5	"	7.061	127.3
Avg.		127.3	bromine value
Std. Dev.		0.75	bromine value
C.V.		0.59	%

5. Outline

(1) Various titration methods for bromine value measurement

The following methods are possible for measurement of bromine value using electrodes for end point detection.

- ① Potentiometric titration method (also called zero-current potentiometric titration method since polarization current is not applied)
- ② Constant-current potentiometric titration method (polarization current is applied and change in potential difference is measured)
- ③ Constant-voltage amperometric titration method (polarization voltage is applied and change in current is measured)

In this measurement, ① Potentiometric titration method and ② Constant-current potentiometric titration were used. As the result of the measurement, ② Constant-current potentiometric titration method was suited for measurement of this sample. Though a clear titration curve was relatively observed in measurement by ① Potentiometric titration method under room temperature, there was a tendency for the titration end point to be unclear when it was measured at 5°C (Figure 1). In general, it is safe to measure bromine value using ② Constant-current potentiometric titration method based on our past experience.

(2) The relationship between bromine addition reaction speed and sample

In general, reciprocal movement in potential occurs frequently as titration approaches the end point in bromine value measurement, and it is assumed that the bromine addition reaction is relatively slow. Therefore, this makes end point detection difficult, while the titration value fluctuates back and forth depending on the titrant dropping control near the end point. As a measure against these problems, cooling of the titrated solution is effective for the purpose of sublimating bromine near the end point and preventing bromine addition to the titration solvent, etc. In addition, some compounds have a slow bromine addition reaction even when they have clear chemical structures and relatively high purities.

Cyclohexane (theoretical bromine value 187 – 199) and diisobutylene (theoretical bromine value 136 – 144) are used for test on bromine value measurement. Though cyclohexane has a relatively fast bromine addition reaction, diisobutylene has a slow reaction. Figure 2 shows the titration curve for cyclohexane measurement with the same conditions as this sample. Since reciprocal movement in potential is small near the titration end point in Figure 2, it is surmised that the reaction speed is high. Diisobutylene indicates a similar tendency to this nonene. Judging from these conditions, the end point condition (control mode) greatly affects the measurement results. In particular, if there are impurities in the sample (sample in which substances with fast and slow bromine addition reaction speeds coexist), it is inevitable for the bromine value to fluctuate depending on the measurement conditions. It is important that measurement be always taken under the identical conditions in quality control analysis, etc.

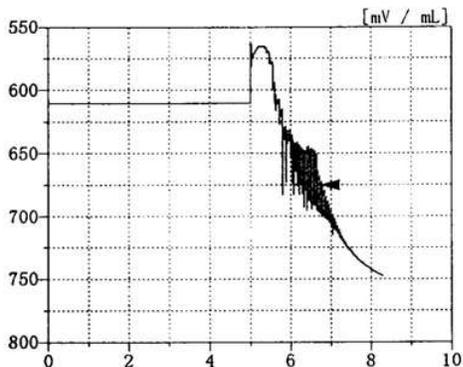


Figure 1: Bromine value titration curve for nonene by potentiometric titration at 5°C.

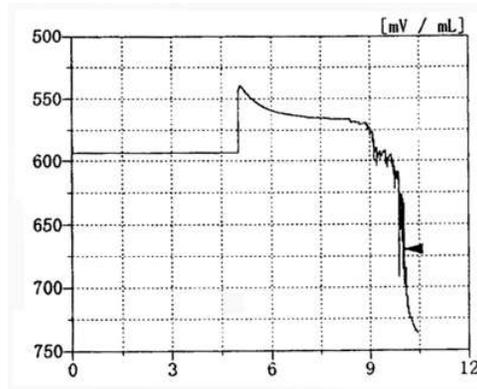


Figure 2: Titration curve for bromine value of cyclohexane

Key words

Nonene, bromine value, constant-current potentiometric titration method

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