Metrohm

Application Bulletin 340 / e

Bromine index (BI) by coulometric titration

Of interest to
General analytical chemistry

Summary

General

This bulletin describes a procedure to determine the bromine index (BI) using coulometric titration.

The bromine index is the fraction of reactive unsaturated compounds (mostly C=C double bonds) in hydrocarbons encountered in the petrochemical industry. The double bonds are split with the attachment addition of bromine:

$$R - C = C - R + Br_2 \rightarrow R - CBr - CBr - R$$

The bromine index (BI) is the number of mg bromine (Br_2) that are bound by 100 g sample.

Generally this method is applicable for olefin-free hydrocarbons with a bromine index lower than 1000.

Products with a bromine index larger than 1000 are typically determined by means of potentiometric titration as the bromine number. However, if longer titration times are acceptable coulometric analysis is possible as well.

The bromine needed for the determination is generated directly in the titration cell by applying a current to the generator electrode. The current releases the stoichiometrically corresponding amount of bromine from the bromide-containing reagent by electrolysis. This means that the coulometric determination of the bromine index is an absolute method – a titer does not need to be determined.

Instruments and accessories

2.851.0010	851 Titrando with generator electrode with diaphragm
2.851.0110	851 Titrando with generator electrode without diaphragm
2.852.0050	852 Titrando with generator electrode with diaphragm
2.852.0150	852 Titrando with generator electrode without diaphragm

Balance	Resolution 0.1 mg

Reagents

Generator electrode with diaphragm

For titrations using the generator electrode with diaphragm the following reagents are used:

Working medium (Anolyte)

600 mL glacial acetic acid

260 mL methanol

Filled up to 1000 mL with aqueous potassium bromide solution, *c*(KBr) = 1 mol/L.

Katholyte

Aqueous potassium chloride solution, *c*(KCl) = 0.2 mol/L.

Generator electrode without diaphragm

For titrations using the generator electrode without diaphragm only one reagent is required:

Working medium

600 mL glacial acetic acid

260 mL methanol

Filled up to 1000 mL with aqueous potassium bromide solution, *c*(KBr) = 1 mol/L

Remark

Generally the reagents are exchanged after addition of approximately 10 mL of sample.

In case the reagent turns turbid, the reagent is exhausted and needs to be exchanged. Discard the contents of the titration vessel and fill it with fresh reagent. In case the generator electrode with diaphragm is used, change the katholyte as well.

Samples

BI standards (10, 100 and 1000) according to ASTM 2710 (Analytical Services, Inc.)

Octene

Decene

Toluene

Sample sizes

Depending on the expected bromine index the sample size should be adapted. The following table shows

Expected bromine index	Redommended sample size
up to 10	2 to 5 g
10 to 100	1 to 2 g
100 to 1000	0.3 to 1 g

Tab. 1: Recommended sample sizes depending on the expected bromine index

Parameters

Generally the following parameters have been used.

I(pol)	1 µA
Generator current[1]	auto mA (with diaphragm) 400 mA (without diaphragm)
Stirring rate	8
Start drift	20 µg/min
Drift correction	off
EP at	200 mV
Titration rate[1]	optimal
Stop criterion	drift & time
Stop drift	15 µg/min
Delay time	40 s

Tab. 2: Parameters for BI determination

[1]There might be the need to adapt the generator current and the maximal titration rate (max. rate) to the sample which is analyzed.

Calculation

The result of the bromine index determination is calculated in mg/100g using the following formula:

$$Bromine\ Index\left[\frac{mg}{100\ g}\right] = \frac{EP \times 0.1}{Sample\ size}$$

EP = bromine, which has been produced to reach the endpoint [µg]
0.1 = calculation factor for mg/100g
Sample size = weight of used sample [g]

Filling of titration vessel

Make sure that the equipment (titration vessel, generator electrode, indicator electrode, …) are clean.

If the generator electrode with diaphragm is used, approximately 100 mL of the working medium are filled into the titration vessel. The generator electrode itself is filled with *c*(KCl) = 0.2 mol/L until working medium and potassium chloride solution have the same level.

With the generator electrode without diaphragm only one reagent is required. To prepare the titration vessel, 100 mL of the working medium are filled into it.

After conditioning – wait until a stable drift of approximately 10 µg/min is reached - the titration vessel is ready for the addition of sample and the subsequent determination of the bromine index.

Examples of application

Different substances with various bromine indexes have been analyzed. Following, examples of titration curves and results of these measurements are shown.

All samples have been measured with a generator electrode with diaphragm, as well as with a generator electrode without diaphragm.

Bromine index standards

Three certified bromine index standard solutions have been analyzed. The standards consisted of cyclohexene and toluene and had BI values of 10, 100 and 1000 respectively.

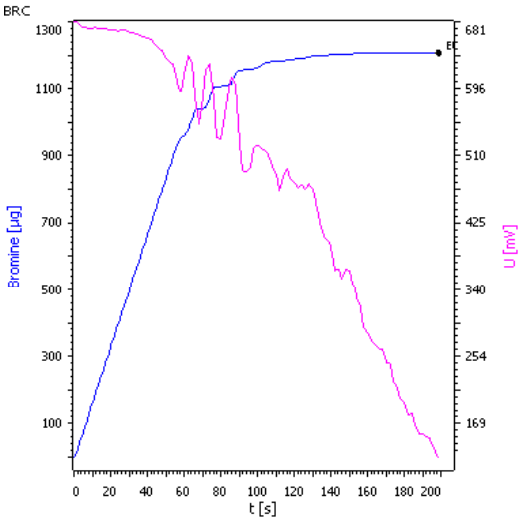

Fig. 1: Titration curve of cyclohexene standard solution (BI 1000) with generator electrode with diaphragm.

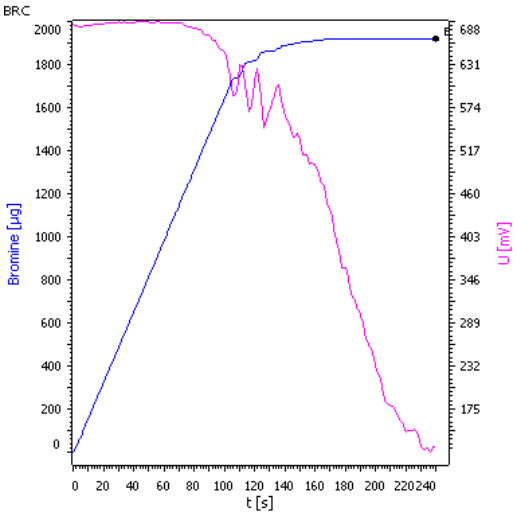

Fig. 2: Titration curve of cyclohexene standard solution (BI 1000) with generator electrode without diaphragm.

Generator electrode with diaphragm:

Sample size [g]	BI [mg/100g]	Sample size [g]	BI [mg/100g]	Sample size [g]	BI [mg/100g]
2.6933	10.53	1.7143	99.34	0.1445	980.05
2.0541	10.59	2.1335	98.83	0.1974	977.74
2.4956	10.54	2.2627	98.59	0.2398	977.70
2.2577	10.63	2.1036	98.72	0.1224	986.06
2.6627	10.67	2.4415	98.48	0.2505	978.90
Mean value	**10.6**		**98.8**		**980.1**
SD	**0.06**		**0.33**		**3.47**
RSD	**0.56**		**0.34**		**0.35**

Tab. 3: Cyclohexen Standard 10, 100 and 1000.

Generator electrode without diaphragm:

Sample size [g]	BI [mg/100g]	Sample size [g]	BI [mg/100g]	Sample size [g]	BI [mg/100g]
2.3335	10.53	1.9641	99.30	0.1458	978.09
2.5055	10.50	2.0677	99.06	0.1963	978.26
2.4255	10.53	2.0471	98.90	0.2115	979.78
2.5476	10.58	2.1616	98.97	0.1847	982.24
2.2755	10.69	2.5692	98.61	0.2626	976.73
Mean value	**10.6**		**99.0**		**979.0**
SD	**0.08**		**0.25**		**2.10**
RSD	**0.71**		**0.25**		**0.21**

Tab. 4: Cyclohexen Standard 10, 100 and 1000.

Octene

To determine the BI value of octene, it was diluted with toluene. The calculated bromine index of the mixture was 543.

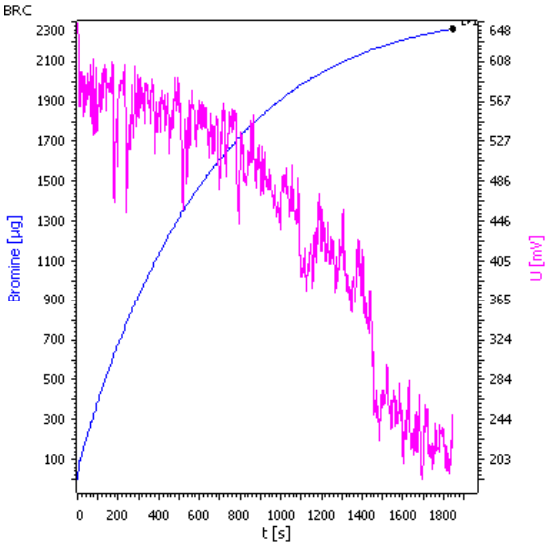

Fig. 3: Titration curve of octene in toluene (BI 543) with generator electrode with diaphragm.

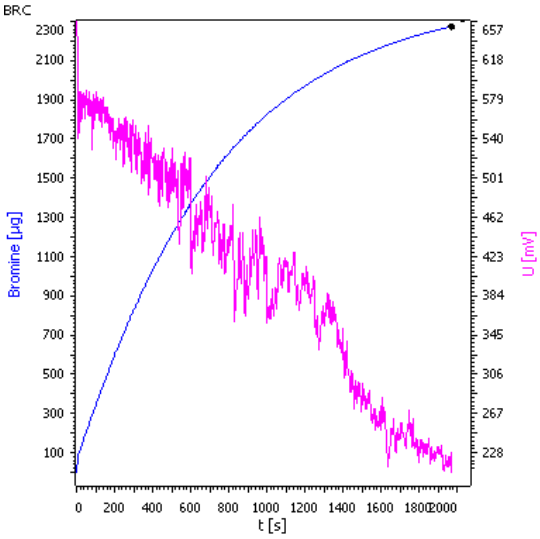

Fig. 4: Titration curve of octene in toluene (BI 543) with generator electrode without diaphragm.

with diaphragm		without diaphragm	
Sample size [g]	**BI [mg/100g]**	**Sample size [g]**	**BI [mg/100g]**
0.4296	527.3	0.4342	523.7
0.3362	513.7	0.4777	518.5
0.3614	526.8	0.3637	535.3
0.3437	518.0	0.3973	517.7
0.2335	518.7	0.3497	542.8
Mean value	**520.9**		**527.6**
SD	**5.93**		**11.03**
RSD	**1.14**		**2.09**

Tab. 5: Results of the octene determination

Decene

To determine the BI value of decene, it was diluted with toluene.
The calculated bromine index of the mixture was 1247.

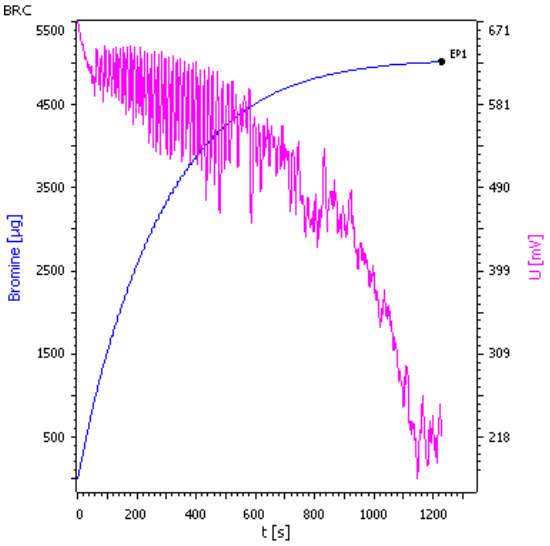

Fig. 5: Titration curve of decene in toluene (BI 1247) with generator electrode with diaphragm.

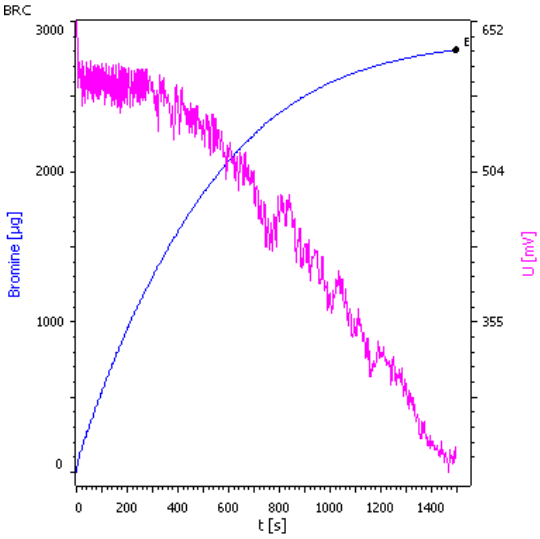

Fig. 6: Titration curve of decene in toluene (BI 1247) with generator electrode without diaphragm.

with diaphragm		without diaphragm	
Sample size [g]	**BI [mg/100g]**	**Sample size [g]**	**BI [mg/100g]**
0.4036	1243.8	0.2252	1247.8
0.1913	1257.6	0.2093	1224.8
0.2360	1234.3	0.2395	1240.7
0.2523	1242.4	0.2142	1228.9
0.3014	1247.5	0.3110	1246.5
Mean value	**1245.1**		**1237.7**
SD	**8.48**		**10.39**
RSD	**0.68**		**0.84**

Tab. 6: Results of the decene determination

Toluene

Toluene was injected directly into the titration vessel.

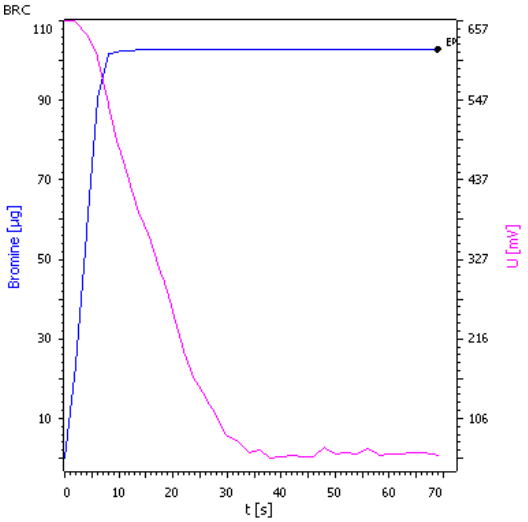

Fig. 7: Titration curve of toluene with generator electrode with diaphragm.

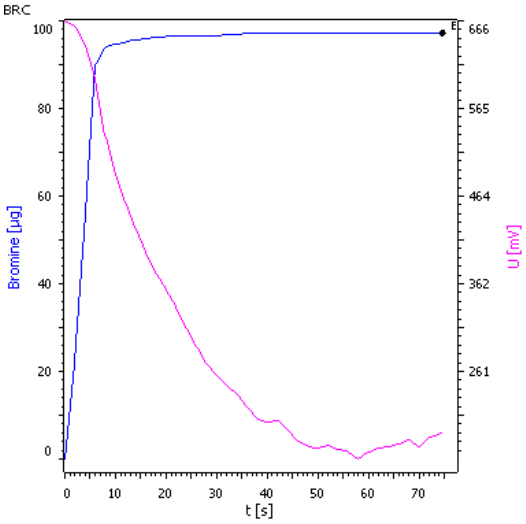

Fig. 8: Titration curve of toluene with generator electrode without diaphragm.

with diaphragm		without diaphragm	
Sample size [g]	**BI [mg/100g]**	**Sample size [g]**	**BI [mg/100g]**
2.3040	4.46	2.3344	4.16
2.2942	4.27	2.2631	4.27
2.3295	4.14	2.2615	4.37
2.2784	4.45	2.2151	4.25
2.2258	4.11	2.3528	4.24
Mean value	**4.3**		**4.3**
SD	**0.17**		**0.08**
RSD	**3.86**		**1.77**

Tab. 7: Results of the toluene determination

Conclusion

Due to the easier handling the use of a generator electrode without diaphragm is recommended for the determination of the bromine index. However, the results show that the bromine index can be determined with both types of generator electrodes (with or without diaphragm).

Literature

ASTM D 1492 – 08, Standard Test Method for Bromine Index of Aromatic Hydrogencarbons by Coulometric Titration