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# Application Bulletin

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Of interest to: Petrochemical industry

G 1, 3, 5

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## Automatic determination of the bromine index and/or the bromine number in petroleum products

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### *Summary*

For both indices standard methods exist, which differ mainly in the composition of the employed solvent mixtures and the concentration of the titrants. The **bromine index** indicates the quantity of bromine in mg that reacts with 100 g of the sample. The **bromine number** indicates the consumption of bromine in g for 100 g sample. Consequently, both indices provide information on the content of substances that react with bromine. Usually these are compounds containing C=C double bonds. A qualitative separation of the different components is not possible with the described method.

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### *Instruments and accessories*

- 702 SET/MET Titrino, 716 DMS Titrino, 736 GP Titrino, 751 GPD Titrino or 785 DMP Titrino or 726 or 796 Titroprocessor with 700 Dosino or 685 Dosimat
- 2.728.0040 Magnetic Stirrer
- 6.3014.213 or 6.3014.223 Exchange Unit
- 6.0308.100 double Pt wire electrode with 6.2104.020 electrode cable
- 6.1110.100 Pt 1000 temperature sensor with 6.2104.080 electrode cable
- 6.1418.250 titration vessel with thermostatic jacket and 6.1414.010 lid
- Thermostat/cryostat

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### *Reagents*

This bulletin does not include advice concerning the use and handling of the described chemicals or the safety precautions to be taken. For this information, we recommend that you refer to the relevant literature.

If possible, one should refrain from using chlorinated solvents. Our investigations have shown that carbon tetrachloride and 1,1,1-trichloroethane can be replaced by diethyl carbonate (Fluka no. 320380, Merck no. 802898).

**Reagents for the determination of the bromine index (mainly small consumption of bromine)**

- Titrant:  
0.02 N bromide-bromate solution [ $c(1/6 \text{ KBrO}_3) = 0.02 \text{ mol/L}$ ]:  
2.04 g KBr and 0.556 g  $\text{KBrO}_3$  are separately dissolved in dist. water. Pour both solutions into a 1000 mL volumetric flask and fill to the mark with dist. water.
- Solvent mixture I (for aliphatic hydrocarbons):  
714 mL glacial acetic acid + 134 mL carbon tetrachloride + 134 mL methanol + 18 mL  $\text{w}(\text{H}_2\text{SO}_4) = 20\%$
- Solvent mixture II (for aromatic hydrocarbons):  
714 mL glacial acetic acid + 134 mL 1-methyl-2-pyrrolidone (Fluka no. 15780, Merck no. 105215) + 134 mL methanol + 18 mL  $\text{w}(\text{H}_2\text{SO}_4) = 20\%$

**Reagents for the determination of the bromine number (mainly large consumption of bromine)**

- Titrant:  
0.5 N bromide-bromate solution [ $c(1/6 \text{ KBrO}_3) = 0.5 \text{ mol/L}$ ]:  
51 g KBr and 13.92 g  $\text{KBrO}_3$  are separately dissolved in dist. water. Pour both solutions into a 1000 mL volumetric flask and fill to the mark with dist. water.
- Solvent mixture:  
714 mL glacial acetic acid + 134 mL 1,1,1-trichloroethane + 134 mL methanol + 18 mL  $\text{w}(\text{H}_2\text{SO}_4) = 20\%$

**Additional reagents**

- Test solution:  
Cyclohexene can be used as a test substance. It has a theoretical bromine number of 194.54 g bromine / 100 g (or a bromine index of 194500 mg bromine / 100 g). However, cyclohexene is never used in pure form, but a solution in 1,1,1-trichloroethane is prepared (e.g. 0.5 g cyclohexene per 50 mL 1,1,1-trichloroethane; 1 mL of this solution then correspond to 10 mg cyclohexene).
- For the titer determination:
  - aqueous potassium iodide solution  $\text{w}(\text{KI}) = 15\%$
  - conc. HCl
  - glacial acetic acid
  - sodium thiosulfate solution  $c(\text{Na}_2\text{S}_2\text{O}_3) = 0.1000 \text{ mol/L}$ , e.g. Merck Titrisol 109950

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**Determination of the titer of the bromide-bromate solutions**

Pour 50 mL glacial acetic acid and 1 mL conc. HCl into an Erlenmeyer flask. Close the flask with a stopper and cool it in an ice bath for 10 min. Then, while tilting the flask back and forth, slowly add 1.00 mL 0.5 N bromide-bromate solution or 25 mL 0.02 N bromide-bromate solution. Now add 5 mL potassium iodide solution, stopper the flask, tilt it back and forth and place it in an ice bath for a further 5 min. Afterwards, add 100 mL dist. water and titrate with  $c(\text{Na}_2\text{S}_2\text{O}_3) = 0.1000 \text{ mol/L}$  using the MET Ipol mode (parameter settings see below).

titer = EP1 / 5

## Analysis

### 1. Determination of the blank

Pour 110 mL solvent mixture into the titration vessel and cool down 0 ... 5 °C, then titrate the blank with the respective titrant (parameter settings see below). The blank (titrant consumption in mL) is stored as common variable C31.

### 2. Determination of the bromine index BI

Pour 110 mL solvent mixture into the titration vessel. Depending on the expected bromine index, add the corresponding amount of sample (see table), cool down to 0 ... 5 °C and titrate with the 0.02 N bromide-bromate solution.

Expected bromine index BI mg bromine / 100 g sample	Sample weight g
0 ... 10	25 ... 30
10 ... 50	15 ... 25
50 ... 100	10 ... 15
100 ... 1000	1 ... 10

Samples with a higher bromine index should first be diluted with carbon tetrachloride.

#### Calculation

$$\text{BI in mg bromine / 100 g sample} = (\text{EP1} - \text{C31}) * \text{C01} * \text{C02} * \text{C03} / \text{C00}$$

EP1 = titrant consumption in mL

C00 = sample weight in g

C01 = 0.02 («normality» of the titrant in mol/L)

C02 = titer of the titrant

C03 = 7990

C31 = titrant consumption for the blank in mL

### 3. Determination of the bromine number BN

#### Sample preparation

Pour 10 mL 1,1,1-trichloroethane into a 50 mL volumetric flask. Depending on the expected bromine number, add 0.5 g ... 20 g sample (see table), fill to the mark with 1,1,1-trichloroethane and mix well.

Expected bromine number BN g bromine / 100 g sample	Sample weight g
0 ... 10	20 ... 16
10 ... 20	10 ... 8
20 ... 50	5 ... 4
50 ... 100	2 ... 1.5
>100	1 ... 0.5



**Figures**

The determinations were carried out using the 736 GP Titrino.

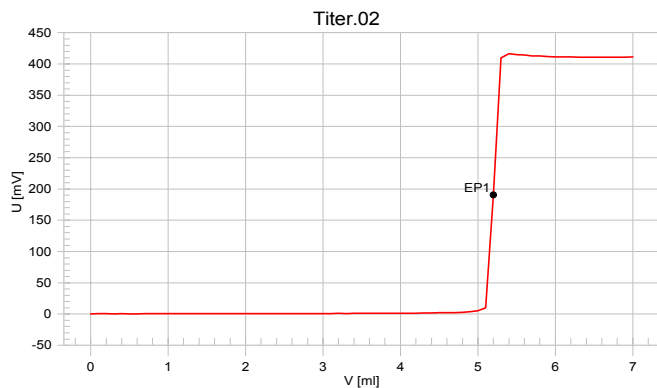
```
'pa
736 GP Titrino      03222  736.0012
date 2000-02-24   time 18:14   11
MET Ipol          Br indBl
Parameters
>titration parameters
  V step           0.02 ml
  titr.rate        max. ml/min
  signal drift     OFF mV/min
  equilibr.time    30 s
  start V:         OFF
  pause           60 s
  dos.element:    internal D0
  I(pol)          1 µA
  electrode test:  OFF
  temperature     8.4 °C
>stop conditions
  stop V:          abs.
  stop V          1 ml
  stop U          OFF mV
  stop EP         9
  filling rate    max. ml/min
>statistics
  status:          ON
  mean            n= 5
  res.tab:        original
>evaluation
  EPC             200 mV
  EP recognition: all
  fix EP1 at U   OFF mV
>preselections
  req.ident:      OFF
  req.smpl size: all
  activate pulse: OFF
-----
```

**Fig. 1:** Parameter settings for the blank determination (bromine index).

```
'pa
736 GP Titrino      03222  736.0012
date 2000-02-24   time 18:17   11
MET Ipol          Br index
Parameters
>titration parameters
  V step           0.05 ml
  titr.rate        max. ml/min
  signal drift     OFF mV/min
  equilibr.time    30 s
  start V:         OFF
  pause           60 s
  dos.element:    internal D0
  I(pol)          1 µA
  electrode test:  OFF
  temperature     4.3 °C
>stop conditions
  stop V:          abs.
  stop V          20 ml
  stop U          OFF mV
  stop EP         9
  filling rate    max. ml/min
>statistics
  status:          OFF
>evaluation
  EPC             200 mV
  EP recognition: all
  fix EP1 at U   OFF mV
>preselections
  req.ident:      OFF
  req.smpl size: value
  activate pulse: OFF
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```

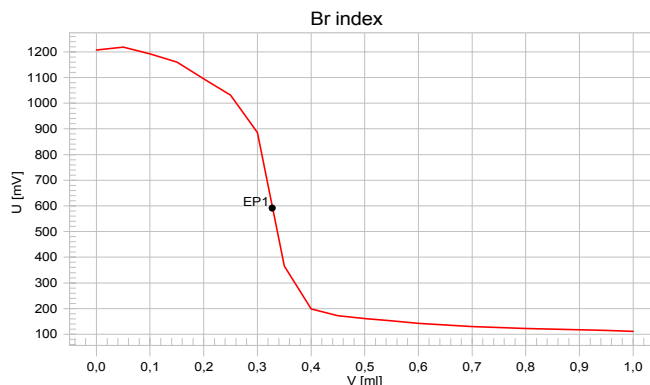
**Fig. 2:** Parameter settings for the determination of the bromine index.

```
'fr
736 GP Titrino      03222  736.0012
date 2000-02-17   time 11:27   1
U(init)           0 mV MET IpolTiter.02
smpl size         25 ml
EP1               5.201 ml      190 mV
Temperat         16.5 C
Titer             1.0402
stop V reached
=====
```



**Fig. 3:** Determination of the titer of the 0.02 N bromide-bromate solution (bromine index).

```
'fr
736 GP Titrimo      03222  736.0012
date 2000-02-24    time 17:38      9
U(init)            581 mV MET IpolBr index
spl size           30.50 g
EP1                0.328 ml          590 mV
Temperat           4.0 C
Br index           1.04 mg/100
manual stop
=====
```



**Fig. 4:** Result block and titration curve for the determination of the bromine index of a heptane sample.

```
'pa
736 GP Titrimo      03222  736.0012
date 2000-02-24    time 18:15      11
MET Ipol           Br numBl
Parameters
>titration parameters
  V step            0.02 ml
  titr.rate         max. ml/min
  signal drift      OFF mV/min
  equilibr.time     30 s
  start V:          OFF
  pause            60 s
  dos.element:     internal D0
  I(pol)           1 µA
  electrode test:  OFF
  temperature      2.4 °C
>stop conditions
  stop V:          abs.
  stop V           0.5 ml
  stop U           OFF mV
  stop EP         9
  filling rate     max. ml/min
>statistics
  status:          ON
  mean            n= 3
  res.tab:        original
>evaluation
  EPC             200 mV
  EP recognition: all
  fix EP1 at U    OFF mV
>preselections
  req.ident:      OFF
  req.spl size:   value
  activate pulse: OFF
-----
```

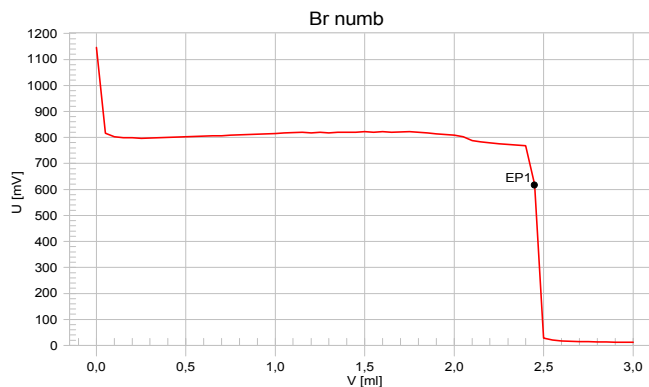
**Fig. 5:** Parameter settings for the blank determination (bromine number).

```
'pa
736 GP Titrimo      03222  736.0012
date 2000-02-24    time 18:16      11
MET Ipol           Br numb
Parameters
>titration parameters
  V step            0.05 ml
  titr.rate         max. ml/min
  signal drift      OFF mV/min
  equilibr.time     30 s
  start V:          OFF
  pause            60 s
  dos.element:     internal D0
  I(pol)           1 µA
  electrode test:  OFF
  temperature      2.4 °C
>stop conditions
  stop V:          abs.
  stop V           3 ml
  stop U           OFF mV
  stop EP         9
  filling rate     max. ml/min
>statistics
  status:          OFF
>evaluation
  EPC             200 mV
  EP recognition: all
  fix EP1 at U    OFF mV
>preselections
  req.ident:      OFF
  req.spl size:   value
  activate pulse: OFF
-----
```

**Fig. 6:** Parameter settings for the determination of the bromine number.

```

'fr
736 GP Titrino          03222  736.0012
date 2000-02-16      time 12:09      7
U(init)              509 mV MET Ipol Br numb
spl size             0.5036 g
EP1                  2.450 ml          616 mV
Temperat             2.4 C
Br numb              189.5 g/100g
stop V reached
=====
    
```



**Fig. 7:** Result block and titration curve for the determination of the bromine number of a cyclohexene solution.

## Literature

- ASTM D 5776-99  
Standard Test Method for Bromine Index of Aromatic Hydrocarbons by Electro-  
metric Titration.
- ASTM D 2710-72  
Standard Test Method for Bromine Index of Petroleum Hydrocarbons by Elec-  
trometric Titration.
- ASTM D 1159-84  
Standard Test Method for Bromine Number of Petroleum Distillates and Com-  
mercial Aliphatic Olefins by Electrometric Titration.
- ISO 3839: 1996  
Petroleum Products – Determination of bromine number of distillates and ali-  
phatic olefins – Electrometric method.