

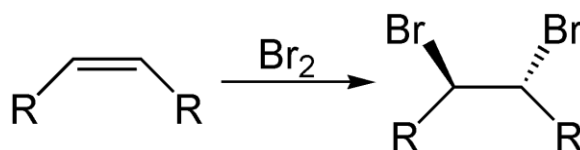
Determination of the Bromine index using coulometric KF-Titrator TitroLine[®] 7500 KF trace

Description

The bromine index is a key figure for the proportion of unsaturated hydrocarbons in various mineral oils. It mainly covers C=C double bonds and reactive compounds that react rapidly with bromine. For this reason, the bromine index is determined by direct titration.

The bromine index is defined as mg bromine / 100g sample and is titrated in samples with low contents. This application note describes the coulometric determination of the bromine index in petroleum products following ASTM D 1492-08.

A defined amount of bromine is added to the sample to be analyzed, and the halogen is added to the C=C double bonds:



In the coulometric bromine index determination, the bromine is generated electrochemically from bromide at a generator electrode. The bromide contained in the reagent is oxidized to bromine at the anode, equivalently H⁺ ions are reduced to hydrogen at the cathode. The end point of the titration is detected with a double platinum indicator electrode. As soon as no more bromine is consumed by the sample, a reversible bromine-bromide redox system is formed, which produces a significant current increase at the polarized indicator electrode. During titration, the coulometer measures the current consumed for bromine generation and the time and calculates from this the amount of bromine generated.

Instruments

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|------------------|--|
| Titration vessel | TZ 1751 (M1) or TZ 1754 (M2) |
| Other items | Desiccant (molecular sieve 4 nm). 100 g are included in the scope of delivery of the accessory kit TZ 1789 (scope of supply of M1 and M2) as well as 1 g glass wool and syringes with cannula. |
| Titration vessel | TZ 1751 (M1) or TZ 1754 (M2) |
| Stirrer | Magnetic stirrer TM 235 (M1) or TM 235 KF (M2) |
| Cable | LB 04 NN |
| Electrodes | KF 1150, generator electrode without diaphragm (both electrodes are included in TL 7500 KF trace M 1 or M 2) |
| Titrator | TL 7500 KF trace M 1 or M 2 |

Reagents

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|---|---|
| 1 | Anolyte/Katholyt: 600 ml glacial acetic acid + 260 ml Methanol + 140 ml 1 mol/L Potassium bromide solution. |
| 2 | Cyclohexen |
| 3 | Toluene |
| | |

Standard preparation

1000 mg/100g Standard:

A glass vessel with lid is placed on the balance and tared. Then approximately 38.52 g of toluene are weighed in. The lid is screwed down and the exact weight is noted. Using a syringe with a needle, approximately 0.2 g of cyclohexene is weighed in without pressing the tare button. The lid is screwed back on and the exact weight is noted. The weighed amount of cyclohexene is calculated from the difference between the weighed-in amount of toluene and the total amount.

The exact bromine index is calculated according to the following formula:

$$BI [mg/100 g] = \frac{amount_{Cyclohexen} [g] \cdot 194531,95}{amount_{Gesamt} [g]}$$

100 mg/100g Standard:

A glass vessel with lid is placed on the balance and tared. Then approximately 18 g of toluene are weighed in. The lid is screwed down and the exact weight is noted. Using a syringe with a needle, weigh in approximately 2 g of the 1000 mg/100g standard without pressing the tare button. The lid is screwed back on and the exact weight is noted. Since this is a 1 in 10 dilution, the bromine index can be calculated using the rule of three. The calculated bromine index of the 1000 mg/100g standard is taken into account accordingly.

Titration procedure

Sample measurement

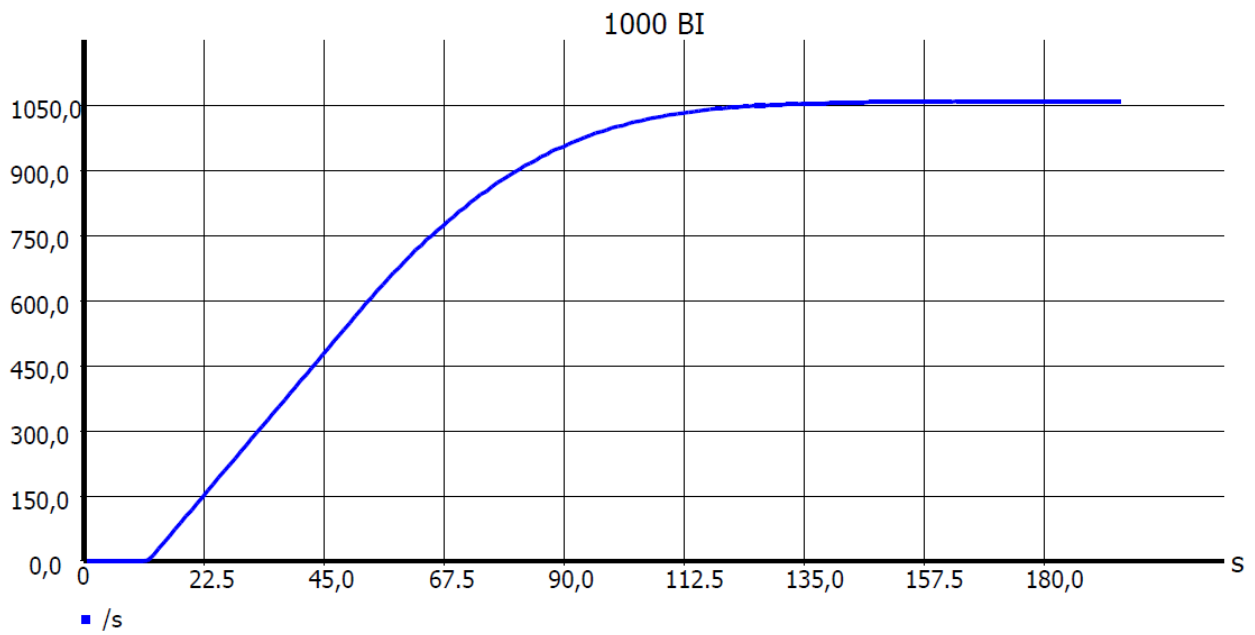
The titration cell is filled halfway with Anolyte/Catolyte reagent (approx. 140 ml) and the coulometer is switched on. The reagent is initialized with a few drops of standard solution until a drift increase is observed. As soon as the drift has returned to a constant value, the sample can be added using a syringe with a cannula. The exact amount of sample is determined by differential weighing. The amount weighed in depends on the expected bromine index and reactivity, so that the resulting titration time is in the range of 3 to 15 min. For samples with a very low content below 10 BI, 5 to 10 g can be weighed in. After adding a total of 10 to 20 ml of sample, the reagent should be renewed.

Note on the working point

With the standard setting <Working point: 300 mV>, it may happen that the titration is terminated slightly too early. This may be caused by sluggish samples, low or very high bromine index contents or a high sample load in the titration cell. In this case, the operating point can be set to 400 mV, which will increase the end point of the titration, causing the titrator to end the measurement later.

Titration parameter

Sample titration



| | |
|-----------------------|--------------------------|
| Default method | Bromine index (coul.) |
| Start drift | 20.0 µg/min |
| Interval | 30 seconds |
| Stability: | 0.5 µg/min |
| Stop drift (delta): | 2.0 µg/min |
| Stop drift tolerance: | 0.02 µg/min ² |
| Stirrer control | free |
| Min. titration time: | 60 seconds |
| Max. titration time: | 1500 seconds |
| Working point: | 300 m |
| Control factor | 4 |

Calculation:

$$Result [ppm] = \mu\text{g} \cdot M \cdot F1 / (F2 \cdot W)$$

| | | |
|---------------|---------|--|
| μg | | Titrated water amount absolute |
| M | 0.88783 | Molecular weight to convert μg water into Bromine |
| W | man | sample weight in g |
| F1 | 1 | Conversion factor |
| F2 | 1 | Conversion factor |

$$Result [\%] = \mu\text{g} * M * F1 / (F2 * W)$$

| | | |
|---------------|---------|--|
| μg | | Titrated water amount absolute |
| M | 0.88783 | Molecular weight to convert μg water into Bromine |
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