

Bromine number and bromine index of petroleum products



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Petroleum products normally consist of a mixture of many different hydrocarbon molecules containing C=C double bonds. The number of double bonds corresponds to the degree of unsaturation. This is an important quality parameter for many raw materials and finished products such as hydrocarbon fuels and lubricants. How is it determined in practice?

Bromine number and bromine index are analytical procedures designed to determine the degree of unsaturation or content of reactive C=C double bonds (olefins) in a hydrocarbon. C=C double bonds can crosslink or react with oxygen to form epoxides, which are also highly reactive. The crosslinking causes the hydrocarbon to form long chain molecules (polymers) which are no longer liquid but solid and are termed gums or varnishes. These form deposits in a fuel system or in a carburetor and can clog up filters and the narrow tubing that supplies fuel to the internal combustion engine. The reduced fuel flow results in a reduction in engine power and might even prevent the engine from starting.

The titration uses a simple reaction

The main reaction in bromine number titration is the addition of one molecule of diatomic bromine to the C=C double bond. One bromine atom adds on each side, one to each carbon atom (Fig. 1). In the titration, bromine is steadily metered in while the level of bromine is detected by a polarized double-pin platinum sensor. When the bromine level is

low, more bromine is added. When no more double bonds are present to react, the level of bromine in the solution rises and the titration is terminated. The amount of bromine added corresponds to the amount of olefin originally present. The bromine number is the quantity of bromine in grams that reacts with 100 grams of sample under the test conditions. The bromine index is the number of milligrams of bromine that react with 100 grams of sample.

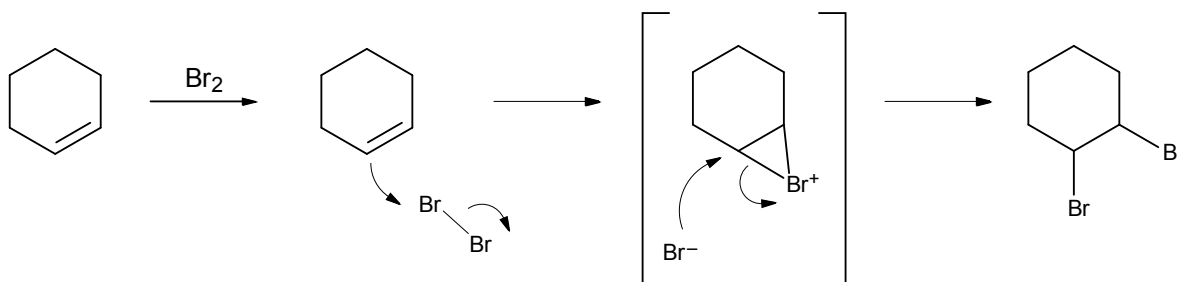
Other reactions in which bromine can participate are oxidation, substitution, and reactions with sulfur, nitrogen or oxygen-containing compounds. The oxidation and substitution reactions occur more slowly at low temperatures. For this reason, the ASTM D1159 (bromine number of petroleum distillates and olefins), ASTM D2710 (bromine index of hydrocarbons) and ASTM D5776 (bromine index of aromatic hydrocarbons by electrochrometric titration) standard test methods are all specified to be conducted at temperatures of 0 to 5 °C. In alpha-olefins, the double bond is between the end carbon and the adjacent carbon. These compounds do not react so readily with bromine and the reaction is incomplete.

Bromine number made easy

The conditions for the potentiometric (electrometric) determination of the bromine number or bromine index include an acidic polar solvent consisting of glacial acetic acid (714 mL), trichloroethane or dichloromethane (134 mL), methanol (134 mL) and sulfuric acid (16.7%, 18 mL). The mixture is held at 0 to 5 °C while a bromide-bromate titrant (KBrO₃ and KBr) is added in small increments. The titration is monitored by a double platinum pin electrode charged positively on one pin and negatively on the other by a constant current. The endpoint is reached when a significant change in potential occurs. A preset endpoint is defined in this region. The titration is terminated when the potential remains the same at this endpoint.

The Excellence titrators are ideal for determining bromine number and bromine index. The One Click shortcut for bromine number makes it easy to start the analysis. The Solvent Manager activates solvent exchange with One Click and so protects the user from contact with the chemicals. The thermostatable beaker keeps the solution between 0 and 5 °C. An external refrigerated circulating ther-

Figure 1: Reaction scheme for the addition of bromine to the double bond of cyclohexene.



mostat is needed for this low-temperature analysis. This applies to the bromine index as well. The method is changed to an EQP (equivalence point) titration for low bromine index levels.

Bromine index – clean and elegant ...

An especially clean, elegant and accurate way to determine the bromine index is to use coulometric titration. The bromine is generated directly in the titration vessel by a current supplied by a platinum-based electrolysis cell instead of through addition from a burette. Fewer chemicals need to be handled and the current generates bromine more accurately than it can be dispensed using a typical burette. The ASTM D1492 standard describes a test method for the coulometric determination of the bromine index at low concentrations. This is performed at room temperature using a fritless electrolysis cell. Typical samples from industry have bromine indices in the range of 2 to 50 for clean aromatic samples such as benzene, toluene, or xylene. The bromine index of raffinates, which are cracked hydrocarbons destined for gasoline production, can be much higher of the order several hundred to several thousand.

The METTLER TOLEDO C30X coulometer is a powerful instrument that can be used to determine the water content of a variety of samples according to Karl Fischer. It also offers a special method for the fast and accurate determination of the bro-

mine index. The control is fast for high values of the bromine index and cautious for small values. This allows accurate and reproducible determination of even low one-digit bromine indices using a mercury-free solvent. The simple method enables determinations to be made without having to develop a specific procedure because predefined method templates can be used. The solvent is blanked out and subsequent samples are all analyzed with the same method.

... and with One Click

The One Click user interface offers direct access to all routine tasks. One click is all it needs to start a method, run a sample or change the solvent. The ingenious design of the coulometric current-electrolysis cell makes cleaning easy and offers high accuracy. The titration vessel is emptied and refilled by activating the Solvent Manager from the titrator. This avoids contact with chemicals. Using the C30 coulometer, you can be sure that your samples meet the technical specifications.

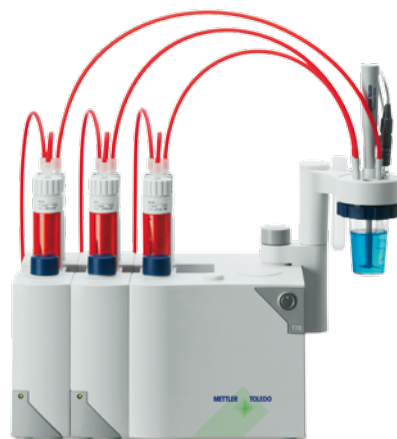


Figure 2: T70 titrator for bromine index and TAN/TBN determination.

Theoretical value	n	Result	srel [%]
141	3	144,2	0,9
8,5	3	10,1	0,3
3,8	3	6,0	1,3
0,9	3	1,9	0,2
Hexan	3	1,4	0,3

Table 1: Results obtained using the C30 coulometer. Samples were cyclohexene diluted with toluene.

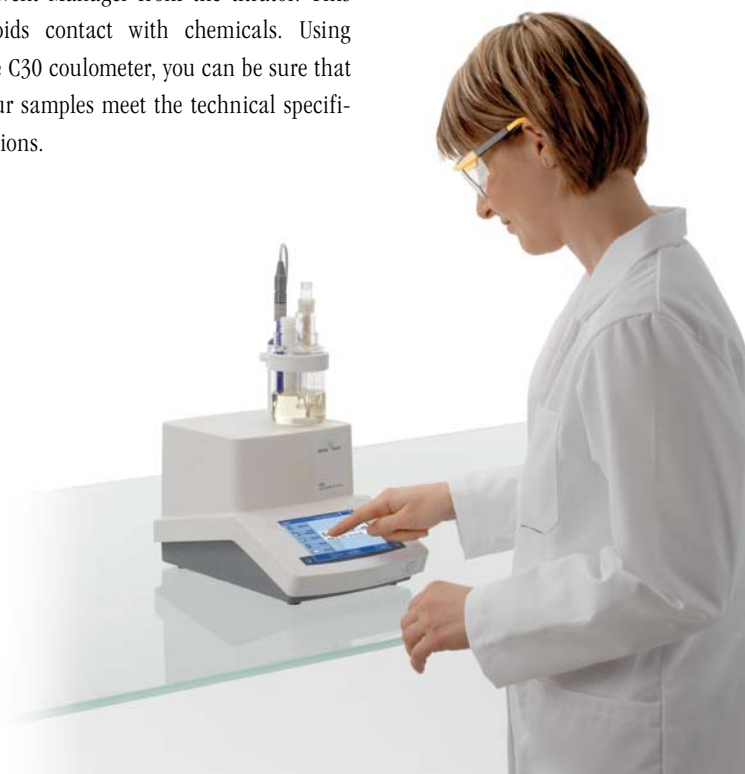


Figure 3: The C30X coulometer in routine use.