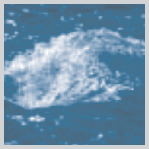
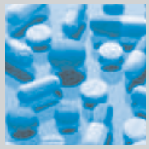
DENVER INSTRUMENT





Bromine Number of Petroleum Products
(ASTM D1159-98 Electrometric titration)

Introduction

This method covers bromine number determination of certain petroleum products indicated in ASTM standard D1159-98. The magnitude of the bromine number is simply an indication of the bromine reactive constituents, not an indication of the constituents. The bromine number mainly indicates the concentration of double bonds present in the product.

Principle

Expressed as g of Bromine (Br_2) able to react with 100 g of product, the bromine number determination uses the reaction between a (Br^-/BrO_3^-) solution and the petroleum product according to the following reactions

a) 5 Br- + BrO3 - + 6H+ .. 3Br2 + 3H2O

b) Br_2 + R-C=C-R ➧ R-C-C-R
| |
Br-Br
(main reaction with product)

(Note that other reactions can occur such as addition, substitution or oxidation)

To avoid secondary reactions the titration is run at low temperature (close to 5°C).

The titrant concentration, expressed as Br_2 concentration, is 0.25 mol/l (or ¼ mol/l). According to reaction (a), the titrant contains 5/12 mole of KBr and 1/12 mol/l of $KBrO_3$. The molar weight of KBr is 119.9 g/mol and for $KBrO_3$ 167.9 g/mol. Titration is run according to an inflection determination with imposed current potentiometry and a double platinum wire electrode.

Electrode and reagents

M241Pt2-8 Metal Electrode, double platinum (part no. E32M002) or M231Pt2 Metal Electrode, double platinum (part no. E32M001) with adapter part no. A94P801 T201 Temperature sensor (part no. E51M001)

Water-jacketed titration beaker connected to a low temperature thermostat or a bath filled with ice
Bromide-Bromate titrant solution (0.25 mol/l as bromine concentration)

Dissolve 51.0 g of KBr (5*119.9/12) and 13.92 g of KBrO3 (167.01/12) in 1000 ml of distilled water using a volumetric flask.

Sulphuric acid (1+5)

Carefully mix one volume of concentrated sulphuric acid with 5 volumes of distilled water. Caution: the dilution reaction is exothermic.

Titration solvent **(see notes)**

Mix 714 ml of glacial acetic acid (CH_3COOH), 134 ml of dichloromethane (CH_2Cl_2), 134 ml of methanol (CH_3OH) and 18 ml of sulphuric acid (1+5).

Dichloromethane (CH_2Cl_2)

Warning: Reagents used in this application note are flammable. They can cause severe burns and are hazardous if swallowed, breathed or come into contact with the skin or eyes. Always respect laboratory health and safety regulations when using these reagents.

Infletion Detection settings

CONTINUOUS IP

Titration with blank	
Burette volume:	10 ml **(see notes)**
Max. volume:	7 ml
Stirring speed:	500 rpm
Working mode:	mV with i >0
Current:	DC
Current value:	5µA **(see notes)**
Blank:	YES
Start timer:	30 s
Stop point:	0 mV
Minimum speed:	0.50 ml/min
Maximum speed:	2.00 ml/min
Smoothing param:	8
Titration:	Decreasing potential
Inflection number:	1
Stop at last IP:	YES
Inflection 1:	
Min. ordinate:	200 mV
Max. ordinate:	800 mV
Sample	
Dilution:	YES
Sample unit:	g
Sample amount:	2 **(see working range)**
Final dilution vol.:	50 ml
Aliquot:	5 ml **(see working range)**

Result 1: ml

Equation 1:
Equation Unit: Bromine number
Equation:
(R1*CT*15.98*DA/(SA*AL)
(see notes)

Procedure

Connect the double platinum wire electrode to the corresponding input of the Titration Manager.

Connect the temperature sensor to the corresponding input on the Titration Manager.

For a new titration solvent batch run a BLANK titration with 115 ml of titration solvent and 5 ml of dichloromethane. The experimental blank volume is generally lower than 0.1 ml.

Sample preparation
Place 10 ml of dichloromethane in a 50 ml volumetric flask then add the weighed sample and fill the flask to the mark with dichloromethane.

Add 110 ml of titration solvent to the titration beaker.

Add an aliquot (generally 5 ml but not more than 10 ml) of the sample solution in dichloromethane.

Dip the electrode, temperature sensor and delivery tip in the beaker and immerse the beaker in an ice bath or alternatively in a low temperature thermostatic bath.

Using the electrode direct measurement function of the Titration Manager (icon ELECTRODES and "DISPLAY MEASUREMENT) allow the solution to reach the mentioned temperature (around 5°C) **(see notes)**.

Run the titration.

Results

As indicated above, results are expressed **in g of Br2 able to react with 100 g of product.**

R(bromine number) =
(Vtitr- Vblk)*C(titr)*159.8*100/ W(smp)*1000

Vtitr = Total volume of titrant used in ml

Vblk = Blank volume used for solvent titration

C (titr) = Concentration of titrant in mol/l

W (smp) = Sample weight in g

159.8 = molecular weight of Br_2

100 = conversion factor for 100 g of product

1000 = correction factor for result in g instead of mg

For 5 determinations on cyclohexene (C_6H_{10})

Mean delivered volume:	3.42 ml
Rel. standard deviation:	1.2%
Corresp. Bromine number:	193
Theoretical:	194.6

Working range

For a sample amount of 1g, and a calculated dilution coefficient of 10 (50 ml for final dilution volume and 5 ml for the aliquot), 1 ml of 0.25 mol/l titrant corresponds to a Bromine number of 37.5.

The magnitude of the bromine number of a sample is often unknown and it is necessary to perform a preliminary test with 2 g of sample.

ASTM Standard D1159 gives a table for sample amount as a function of Bromine number:

Bromine number	Sample amount in g	Titrant volume in ml
0-10	20-16	Around 4
10-20	10-8	Around 3-4
20-50	5-4	Around 5
50-100	2-1.5	Around 4
100-150	1.6-0.8	Around 3-4
150-200	0.8-0.6	Around 3-4

Notes

Notes regarding the titration solvent
ASTM Standard D1159 gives trichloroethane as an alternative for dichloromethane. However, the use of this solvent is forbidden in many countries. To save time, you can store the titration solvent in a refrigerator between the experiments.

Note regarding the maximum volume
To avoid a two-phase system during titration, it is not recommended to use a titrant volume higher than 10 ml.

Note regarding the imposed current
A 1 µA imposed current can give noisy curves and 10 µA gives a curve that is not well defined around the inflection point. Instead of DC imposed current it is possible to use AC imposed current. A 25 µA AC imposed current gives titration curves similar to those obtained with 5 µA DC current. In this case, also modify the "Br- Nb-Ctrl-Temp" method.

Note regarding the equation
The entered equation takes into account the programmed dilution of the sample. DA is the final dilution volume and AL the aliquot volume.

Note regarding sample handling
For sample and dichloromethane handling, you can use a glass syringe instead of a pipette.

Note regarding temperature measurement
As indicated previously, you can use the DISPLAY MEASUREMENT function, but in this case you can just check the temperature of the solution (DISPLAY MEASUREMENT checks the measured potential on E1 and E2 inputs, not on Pt-Pt input). You can use this information in the pre-programmed method "Br- Nb-Ctrl-Temp" that measures the potential of the double platinum wire electrode AND the sample temperature.

Note regarding the curve shape
Based on experience, the starting potential may be around 1300 mV and suddenly falls to around 800 mV

at the beginning of the titration. Then the curve falls very quickly to the final measured potential (generally around 100 mV) near the inflection point.

Curve