

Based on ASTM D1159 – 07 (2012)

Potentiometry with Imposed Current: Forward Titration
0.500 – 200 g/100 g as Br₂

1. Introduction

This application note follows the ASTM norm D1159- 07 (2012). It deals with the determination of the Bromine Number of petroleum distillates and commercial aliphatic olefins by an electrometric titration with imposed current.

The Bromine Number is an indication of the aliphatic unsaturation present in petroleum samples. The magnitude of Bromine Number is simply an indication of the bromine reactive constituents, not an indication of the constituents.

The Bromine Number is expressed as g of bromine (Br₂) able to react with 100 g of product.

2. Principle

In this procedure, we use the reaction of a Br⁻/BrO₃⁻ mixture with the double bond present in the product.

The reaction takes place into two steps:

- 1) $5\text{Br}^- + \text{BrO}_3^- + 6\text{H}^+ \rightarrow 3\text{Br}_2 + 3\text{H}_2\text{O}$
- 2) $\text{Br}_2 + \text{R}-\text{C}=\text{C}-\text{R} \rightarrow \text{R}-\text{CBr}-\text{CBr}-\text{R}$

The first reaction creates in the beaker, the titrant needed to react with the double bond (second reaction). In order not to have secondary reactions, the complete titration must be done below 5 °C in a water-jacketed titration beaker connected to a thermostatic bath.

In the working range, the sample (weighed) is diluted into dichloromethane, and an aliquot of this sample solution is titrated.

3. Electrode and reagents

Intellical MTC695: PtPt-electrode with temperature sensor

Titant: Bromide/Bromate 0.25M as Br₂: Dissolve 51.0 g of KBr with 13.92 g of KBrO₃ in 1000 mL of distilled water in a volumetric flask class A.

Titration solvent: Mix 714 mL of glacial acetic acid (CH₃COOH), 134 mL of dichloromethane (CH₂Cl₂), 134 mL of methanol (CH₃OH) and 18 mL of sulfuric acid (1+5). As 110 mL of this solvent is used for each analysis it is strongly recommended to prepare more than 1 liter of titration solvent. This solvent will have to be stored in a fridge to quickly reach the right temperature for the titration.

Sulfuric acid (1+5): Carefully mix 1 volume of concentrated sulfuric acid with 5 volumes of distilled water. Care must be taken as the reaction is exothermic. To calibrate the Bromide/bromate titrant solution, use this titrant as sample and use a sodium thiosulfate 0.1 N solution as titrant. Use the Calibration Br/BrO₃ application associated with this application. For this calibration the following is required:

Na₂S₂O₃ standard solution 0.1 N: It is strongly recommended to buy a commercially available standard solution and to enter the titer indicated by the manufacturer.

Potassium iodide solution (150 g/L): Dissolve 75g of KI in 500 mL of distilled water using a volumetric flask.

Concentrated hydrochloric acid

Description	Qty. required per test
Required apparatus	
Water- jacketed beaker, glass, 120 mL	1
Cylinder, graduated, 250 mL	1
Magnetic stir bar, Teflon® coated	1
Thermostatic bath able to go down to 5 °C	1
Optional apparatus	
Mini-printer, with cable	1

4. Ranges and settings

4.1. Default parameters

The working procedure is described using the following parameters and a syringe volume of 10 mL:

Bromine number	Specimen size	Unit
0 to 10	20 to 16	[g]
Over 10 to 20	10 to 8	[g]
Over 20 to 50	5 to 4	[g]
Over 50 to 100	2 to 1.5	[g]
Over 100 to 150	1.0 to 0.8	[g]
Over 150 to 200	0.8 to 0.6	[g]

4.2. Working ranges

This procedure is aimed at a determination of Bromine Number from 0.5 to 200 g/100 g.

For lower concentrations and for higher accuracy of Bromine Number below 1 g/100 g, it is recommended to use the ASTM norm D2710-09. This norm is not developed within this application note.

4.3. Settings

Name	Default parameter	Unit
Application		
Application name	Bromine Number 0.5 to 200 g/100 g	
Sample		
Name	Sample	
Amount	2.000	[g]
Probe		
Recommended probe	MTC695	
Measurement type	mV	
Working mode	Alternating imposed current	
Imposed current	20	[μ A]
Titrant		
Name	Br/BrO ₃	
Titrant concentration	0.2500	[mol/L]
Syringe	Syringe 1	
Automatic addition (titration solvent)		
Active	No	
Time	70	[s]
Stirring speed	30	[%]
Pump	Pump1	
Manual addition (titration solvent)		
Active	Yes	
Message	Add 110 mL of cold titration solvent	
Stirring speed	30	[%]
Sample addition		
Active	Yes	
Message	Add 5 mL of prepared sample (or 5 mL of solvent if blank)	
Stirring speed	30	[%]
Temperature stabilization		
Active	Yes	
Message	Press Skip when T °C is below 5 °C	
Time	600	[s]
Stirring speed	30	[%]
IP titration		
Stirring speed	30	[%]
Measured parameter		[mV]
Predose	0	[mL]
Max volume stop point	7	[mL]

Stop on last EQP	Yes	
Delay	0	[s]
Min increment size	0.01	[mL]
Max increment size	0.1	[mL]
Result 1 name		
Hide	Yes	
R1 resolution	2 decimals	
R1 min	0.01	[mg/g]
R1 max	300	[mg/g]
R1 QC min	0.01	[mg/g]
R1 QC max	300	[mg/g]
R1EQP index	1	
R1 molar weight	159.8	[g/mol]
Exchange electron Sample	2	
Exchange electron Titrant	2	
Equation 1 name	Bromine number	
Hide	No	
R1 resolution	1 decimal	
Unit	g/100 g	
Equation	R1 x 0.1 x FX	
Eq1 min	0.0	[g/100 g]
Eq1 max	250	[g/100 g]
Fx	10	

5. Titration procedure

5.1. Sample tips and technique

The sample needs to be diluted prior to titration. For this purpose, in a 50 mL volumetric flask weigh the sample following the indication found in section [4.1 Default parameters](#) if the expected Bromine Number is known. If not known, weigh 2 g of sample and note precisely the value. Dilute to 50 mL with dichloromethane.

For better accuracy, when a better estimation of the Bromine Number range of the sample is known, adjust the sample amount.

For the titration take precisely 5 mL of this prepared solution. At the end of the titration, enter the weight of sample noted. The dilution of the sample has been taken into account in the equation with the factor Fx:

$$R1 \times 0.1 \times Fx$$

Where:

- R1 is expressed in mg/g of product
- 0.1 represents the conversion of mg/g into g/100 g: x100 for 100 g of product and /1000 for mg into g
- Fx here equals 10, as 5 mL of aliquot taken out of 50 mL dilution: 50/5

Modify this factor if the sample is diluted differently.

Prior to any titration or when using a newly made titration solvent, it is possible to perform a blank determination. For this, in the titration screen for the sample type, chose **Determine blank**.

Instead of adding 5 mL of the sample, add 5 mL of dichloromethane (or the sample solvent used in dilution).

The blank volume should be less than 0.1 mL. If not prepare a new titration solvent or a new titrant.

After determination of the blank value, always choose **Sample with blank** for the sample type, in order to have the blank volume subtracted from the titration volume.

The inflexion point is very sharp. In order not to exceed this point, parameters must be set to go slowly in volume increment and the measurement stabilization time. For the settling time to reach the correct temperature and titration, the elapsed time could be up to 20 minutes.

5.2. Reagent tips and technique

- Bromide/bromate solution is a stable solution. However, if calibration is needed, please refer to section 9 **Appendix: Titrant Calibration**.
- Rinse the beaker after each titration and dry it.
- Rinse the electrode, temperature probe and injection tip with deionized water before every titration and dry them with a tissue.

5.3. Instrument tips and technique

- A distinction is drawn between running a new test and a new sample (**Exit** or **Next**). Pushing **Next** is a replicate run of the current or previous sample analysis. The titrator automatically tracks the results of a series of tests, and automatically calculates the mean and standard deviation for all the results.
- The TitraLab AT1000 Series instrument calculates the chlorine concentration based on the sample amount. Make sure that the sample amount is correct.
- Press the **Stop** key at any time to interrupt the operation.
- Flush the syringe each day before the first sample test or before a calibration is performed.
- Flush the syringe when changing titrants.

5.4. Cleaning and storage

- Clean the MTC695 electrode when needed (e.g. after a titration when the equivalent point is not detected). Refer to the cleaning instructions delivered with the electrode.
- For long term storage period (e.g. more than 3 days) rinse the electrode, dry gently with a tissue and store dry in the electrode protector.

5.5. Safety

- Use good safety practices and laboratory techniques throughout the procedure. Consult the Material Safety Data Sheet (MSDS) for specific reagent information.
- Flammable solvents are being used. They can cause severe burns and are hazardous if swallowed. Always respect laboratory health and safety regulations when using these reagents.

5.6. Analysis steps

1. In the **Main** menu, highlight Bromine N° 0.5-200g/100g and press **Start**.
2. Verify the **Operator Name** and the **Sample Name**. Modify them if necessary.
3. Select the appropriate sample type. If this is the first experiment or the renewal of the titration solvent, select **Determine blank**. If the blank has already been determined, select **Sample with blank**. Make sure that the sample preparation is ready and the thermostatic bath is set to 4-5 °C.
4. Place the water-jacketed beaker onto the TitraLab AT1000 Series platform with the stirrer and press **Start**. Follow the instructions on the display.
5. Add 110 mL of titration solvent. Note that the solvent is added to adjust the sample pH and dissolved. The precise amount added is not crucial for the accuracy or precision of the analysis.
6. Add 5 mL of sample or solvent for the blank. Use a precise syringe to do so. This is crucial for the results. Lower the electrode head onto the beaker.
7. The settling timer begins, allowing the mixture to reach a temperature below 5 °C. Measurement is displayed during this time. When the temperature is below 5 °C press **Skip** to start the titration. This is crucial to avoid any side reaction of Bromine.
8. The titration curve will appear on the display. The instrument performs the analysis based on the automatic determination of the inflection point.
9. When the analysis for this test is complete, the instrument asks for the sample amount weighed during the preparation of the sample. Press **OK** for the results. Press **Next** for a replicate measurement or for a new measurement on a different sample, or press **Exit** to go back to main menu.
10. If the expected concentration of the sample is known and a reduction in the titration time is required, modify the method and add a pre-dose at the beginning of the titration. However always leave at least 0.5-1 mL before the end point.

6. Results

6.1. Result calculation

$$\text{Bromine } N^{\circ} = \frac{(V_{\text{titrant}} - V_{\text{blank}}) (\text{ml}) \times C_{\text{titrant}} (\text{mol/L}) \times M_{\text{Br}_2} (\text{g/mol}) \times F_x \times 100}{1000 \times W (\text{g})}$$

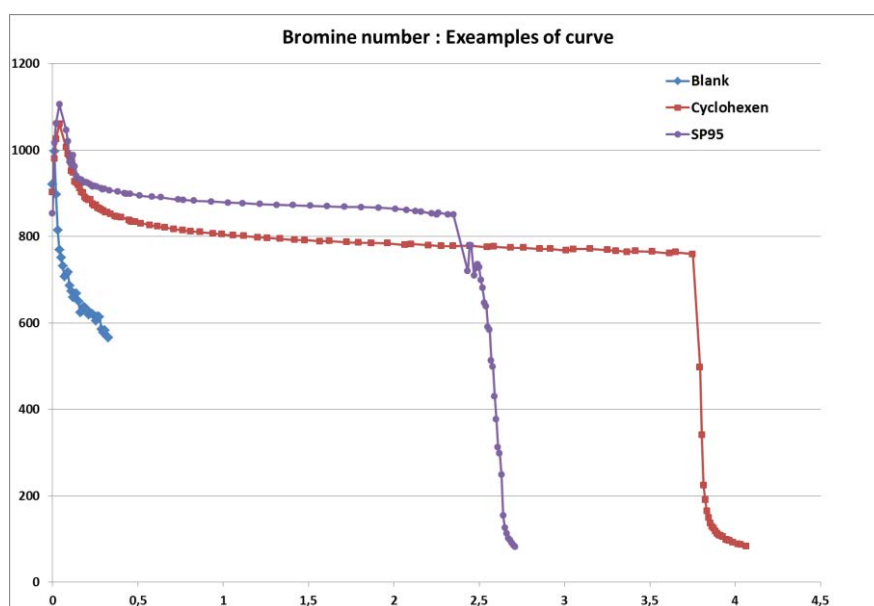
6.2. Experimental results

These results are indicative and have been obtained for a given known sample and gasoline SP95. Depending on the expected value of Bromine Number, the sample amount has been set according to the table found in section 4.1 Default parameters: Cyclohexene (0.8 g) and SP95 (5 g).

Cyclohexene (194.6 g/100 g) (4 replicates)	
Mean Bromine Number (g/100 g)	193.5
Standard deviation (g/100 g)	3.0
Relative standard deviation (%)	1.6
Accuracy (%)	0.9

Gasoline SP95 (9 replicates)	
Mean Bromine Number (g/100 g)	20.9
Standard deviation (g/100 g)	0.55
Relative standard deviation (%)	2.6

6.3. Examples of the titration curve



7. Recommendations

Store the titration solvent in a refrigerator in order to reach the titration temperature as quickly as possible. A settling time of 10 minutes has been programmed by default but can be skipped if the temperature is already reached. After 10 minutes, the titration will start regardless of temperature. Make sure to modify this time if necessary, as it is important to perform the titration below 5 °C.

8. Bibliography

- ASTM D1159-07 (2012)

9. Appendix: Titrant calibration

The bromide-bromate titrant solution cannot be calibrated directly. It has to be used as a sample in an application using sodium thiosulfate as the titrant.

To calibrate the Bromide-Bromate solution, install the Cal Br-BrO₃ Titrant application on the instrument. It may require uninstalling an existing and to installing the application. Please refer the user manual for these recommended actions.

Preparation of the sample has to be performed quickly and to set at a temperature below 20 °C. It is possible to have the waiting time for the mixture of the sample preparation within the application.

After the determination of the Bromide-Bromate solution titer, enter the result of this application into the Bromine Number 0.5-200 g/100 g application. For this the application will have to be reinstalled on the instrument unless it is a bi-burette instrument.

To enter the new titer of the Bromide-Bromate solution, edit the Bromine Number application and enter the titer in the titrant section.

9.1. Analysis steps

1. In the **Main** menu, highlight **Calibration Br-BrO₃** and press **Start**.
2. Verify the **Operator Name** and the **Sample Name**. Modify them if necessary.
3. Place the water-jacketed beaker onto the TitraLab AT1000 Series stirrer platform with the stirrer and press **Start**. Follow the instructions on the display.
4. Add 50 mL of glacial acetic acid. Note that the precise amount added is not crucial for the accuracy or precision of the analysis.
5. Add 1 mL of concentrated hydrochloric acid.
6. Add precisely 1 mL of the Bromide-Bromate solution. This is crucial for the results. Use a precise syringe to do so. Cover the beaker for the time it takes to prepare the next addition.
7. Add approximately 1 mL of potassium chloride (150 g/L). Cover the beaker.
8. Add approximately 50 mL of deionized water, and lower the electrode head onto the beaker.
9. A pre-dose has been programmed in order to speed up the titration time.
10. The titration curve will appear on the display. The instrument performs the analysis based on the automatic determination of the inflection point.
11. When the analysis for this test is complete, press **Next** for a replicate measurement or for a new measurement on a different sample, or press **Exit** to go back to main menu.

9.2. Settings

Name	Default parameter	Unit
Application		
Application name	Cal Br-BrO ₃ titrant	
Sample		
Name	Sample	
Amount	1.000	[mL]
Probe		
Recommended probe	MTC695	
Measurement type	mV	
Working mode	Alternating imposed current	
Imposed current	10	[μA]
Titrant		
Name	Na ₂ S ₂ O ₃	
Titrant concentration	0.100	[eq/L]
Syringe	Syringe 1	
Manual addition (acetic acid)		
Active	Yes	
message	Add 50 mL acetic acid	
Stirring speed	30	[%]
Manual addition (hydrochloric acid)		
Active	Yes	
Message	Add 1 mL of hydrochloric acid	
Stirring speed	30	[%]

Sample addition		
Active	Yes	
Message	Add 1 mL of sample	
Stirring speed	30	[%]
Manual addition (KI)		
Active	Yes	
Message	Add 1 ml of KI solution	
Stirring speed	40	[%]
Manual addition (deionized water)		
Active	Yes	
Message	Add 50 ml of DI water, lower head and press OK	
Stirring speed	30	[%]
IP titration		
Stirring speed	30	[%]
Measured parameter		[mV]
Predose	3.5	[mL]
Max volume stop point	10	[mL]
Delay	0	[s]
Stop on last EQP	Yes	
Min increment size	0.01	[mL]
Max increment size	0.1	[mL]
Result 1 name	Br-BrO3 titer	
R1 resolution	4 decimals	
R1 min	0.24	[mol/l]
R1 max	0.26	[mol/l]
R1 QC min	0.1	[mol/l]
R1 QC max	0.5	[mol/l]
R1EQP index	1	
R1 molar weight	159.8	[g/mol]
Exchange electron Sample	2	
Exchange electron Titrant	1	