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Bromine Number and Bromine Index of Hydrocarbons by Potentiometric Titration

UOP Method 304-08

Scope

This method is for determining bromine number and bromine index, by potentiometric titration, in hydrocarbons that are stable at room temperature and have endpoints below 550°C (1022°F) as determined by ASTM Method D 1160, “Distillation of Petroleum Products at Reduced Pressure,” or D 2887, “Boiling Range Distribution of Petroleum Fractions by Gas Chromatography.” The results denote those compounds that react with bromine under the analytical conditions prescribed in this method, and, in general, are relatable to olefin content. However, certain non-olefinic compounds can constitute a positive interference, while some olefins will not react stoichiometrically (see ASTM D 1159, “Bromine Number of Petroleum Distillates and Commercial Aliphatic Olefins by Electrometric Titration”). The olefin content can be estimated using the calculation in ASTM D 1159.

References

ASTM Method D 1159, “Bromine Number of Petroleum Distillates and Commercial Aliphatic Olefins by Electrometric Titration,” www.astm.org

ASTM Method D 1160, “Distillation of Petroleum Products at Reduced Pressure,” www.astm.org

ASTM Method D 1492, “Bromine Index of Aromatic Hydrocarbons by Coulometric Titration,” www.astm.org

ASTM Method D 2710, “Bromine Index of Petroleum Hydrocarbons by Electrometric Titration,” www.astm.org

ASTM Method D 2887, “Boiling Range Distribution of Petroleum Fractions by Gas Chromatography,” www.astm.org

ASTM Method D 5776, “Bromine Index of Aromatic Hydrocarbons by Electrometric Titration,” www.astm.org

UOP Method 999, “Precision Statements in UOP Methods,” www.astm.org

Outline of Method

The sample is dissolved in a titration solvent containing a catalyst that aids in the titration reaction. The solution is titrated potentiometrically at room temperature with either a 0.5-*N* (0.25-*M*) or 0.02-*N*

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(0.01-M) bromide-bromate solution depending upon whether bromine number or bromine index, respectively, is being determined. The titration uses a combination platinum electrode in conjunction with a recording potentiometric titrator. Bromine number or index is calculated from the volume of titrant required to reach a stable endpoint.

Definitions

Bromine number, the number of grams of bromine consumed by 100 g of the sample when reacted under the conditions specified.

Bromine index, the number of milligrams of bromine consumed by 100 g of the sample when reacted under the conditions specified. By definition the bromine index divided by 1000 is essentially equivalent to the bromine number.

Other methods for the determination of bromine index or bromine number, that may be useful for reference purposes, include: ASTM Method D 1159, "Bromine Numbers of Petroleum Distillates and Commercial Aliphatic Olefins by Electrometric Titration," ASTM Method D 1492, "Bromine Index of Aromatic Hydrocarbons by Coulometric Titration," ASTM Method D 2710, "Bromine Index of Petroleum Hydrocarbons by Electrometric Titration," and ASTM Method D 5776, "Bromine Index of Aromatic Hydrocarbons by Electrometric Titration."

Apparatus

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Balance, readability, 0.1-mg

Beaker, 250-mL, tall, without spout, borosilicate glass, Wilmad-LabGlass, Cat. No. G-9906-002

Cylinders, graduated, Class B, 25-, 50-, 100-, and 1000-mL, VWR, Cat. Nos. 89001-112, -114, -116, and -122, respectively

Electrode, platinum ring, combination, Metrohm USA, Cat. No. 020924357. See *Note 1*.

Flasks, volumetric, Class A, 100- and 1000-mL, VWR, Cat. Nos. 89001-964 and -966, respectively

Pipets, volumetric transfer, Class A, 20- and 100-mL, VWR, Cat. No. 89002-762 and -768, respectively

Pipet filler, VWR, Cat. No. 53497-055

Refrigerator, hazardous location or flammable storage, VWR, Cat. No. VF-6EAR

Stir bar, Teflon™ coated, VWR, Cat. No. 58948-950

Stirrer, magnetic, VWR, Cat. No. 11301-010

Titration, potentiometric, recording, ± 2000 -mV range, 1-mV resolution, capable of following a maximum allowable drift throughout a titration and/or reducing the titration rate to a minimum in the vicinity of the equivalence point, with dispenser having a volume readout of 0.001-99.999 mL with a 0.0001 of the buret volume resolution, Metrohm 835 Titrando™ system with optional 814 sample changer, and 1-, 5-, and 10-mL burets.

Reagents

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used. References to water mean double-deionized or triple-distilled water.

Acetic acid, glacial, 99.7% minimum purity, VWR, Cat. No. EM-AX0074-2

Cyclohexene, 99+% minimum purity, VWR, Cat. No. AA32673-K2

Cyclohexene-Bromine Number reference standard solution. Weigh, to the nearest 0.1 mg, 1.78 g of cyclohexene into a 100-mL volumetric flask, tared to the nearest 0.01 g. Dilute to the mark with toluene, mix well and reweigh. Calculate the theoretical bromine number (Equation 1). Store the solution in the refrigerator when not in use. When refrigerated, the solution is stable for 6 months.

Cyclohexene-Bromine Index reference standard solution. Weigh, to the nearest 0.1 mg, 4.33 g of cyclohexene Bromine Number reference standard solution into a 100-mL volumetric flask, tared to the nearest 0.01 g. Dilute to the mark with toluene, mix well and reweigh. Calculate the theoretical bromine index (Equation 2). Store the solution in the refrigerator when not in use. When refrigerated, the solution is stable for 6 months.

Mercuric chloride, powder, 99.5% minimum purity, VWR, Cat. No. EM-MX0345-4

Mercuric chloride methanolic solution. Weigh 10.00 ± 0.01 g of mercuric chloride powder into a 100-mL volumetric flask. Dilute to the mark with methanol. Mix well.

Methanol, 99.8% minimum purity, VWR, Cat. No. BJ230-1

Methylene chloride, 99.9% minimum purity, unstabilized, Fisher Scientific, Cat. No. D150SK-1 (see Note 2)

Potassium bromide, crystal, 99.0% minimum purity, VWR, Cat. No. EM-PX1380-1

Potassium bromide, 30% solution. Dissolve 30 ± 0.01 g of potassium bromide in 80 mL of water in a 100-mL volumetric flask. Dilute to the mark and mix well.

Potassium bromide-bromate solution, certified, 0.5-N (0.25-M), as generated bromine (Br_2), Lab Chem, Inc., Cat. No. LC11970-1. See the *Appendix* for an alternative procedure to prepare and standardize this solution in the laboratory.

Potassium bromide-bromate solution, 0.02-N (0.01-M), as generated bromine (Br_2). Pipette 40 mL of 0.5N bromide-bromate solution into a 1000-mL volumetric flask. Dilute to the mark with water and mix well (see *Standardization of Titrant*).

Sulfuric acid, approximately 6-N (3-M), VWR, Cat. No. VW3485-1

Stopper, silicone rubber, VWR, Cat. No. 59590-084

Syringes, disposable, all PP/PE, 5-, 20-, and 50-mL. VWR, Cat. Nos. 53548-004, -008, and 010, respectively, with needle, VWR, Cat. No. BD305187. These syringes must not have rubber tips, nor contain silicone oil.

Titration solvent-bromine index. Prepare one liter of titration solvent by mixing the following in a 1000-mL volumetric flask, in the order shown. The solution must be mixed well after each addition: 704 mL of glacial acetic acid, 134 mL of methylene chloride, 98 mL of methanol, 18 mL of 3-M sulfuric acid, 36 mL of methanolic mercuric chloride and 10 mL of 30% potassium bromide solution (see Note 3). Allow to stand overnight before use. Titration solvent cannot be stored longer than one week.

Titration solvent-bromine number. Prepare one liter of titration solvent by mixing the following in a 1000-mL volumetric flask: 714 mL of glacial acetic acid, 134 mL of methylene chloride, 116 mL of methanol, 18 mL of 3-M sulfuric acid and 18 mL of methanolic mercuric chloride. Allow to stand overnight before use. Titration solvent cannot be stored longer than one week.

Toluene, high purity, VWR, Cat. No. BJ347-4

Vials, glass, with polyseal cone lined caps, 15-mL, VWR, Cat. No. 16087-062

Water, double-deionized or triple-distilled

Wiper, Kimwipes, VWR, Cat. No. 21905-026

Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of titration, and with the equipment being used.

Electrode Preparation and Blank

The electrode must be properly conditioned to obtain reproducible and noise-free titration curves. Condition the electrode at the beginning of each day, or if 2 or more hours have elapsed between sample titrations, by titrating a minimum of 2 blank determinations. Use the procedure described under *Determination of Bromine Index* or *Determination of Bromine Number* except that no sample is added. The results from the two blanks are compared and if they are within 0.02 mL, samples can be analyzed. If the two blanks do not agree within 0.02 mL, the blank titration must be repeated. If the blanks do not consistently repeat within 0.02 mL, reanalyze the blank after every sample. Use the average of the blank titration results, before and after the sample titration, in the calculation.

Standardization

Calculate the theoretical bromine number to one decimal place for the dilute Cyclohexene-Bromine Number reference standard solution using Equation 1:

$$\text{Theoretical Bromine Number} = 194.556 \frac{B}{X} \quad (1)$$

where:

B = mass of cyclohexene, g

X = mass of cyclohexene plus toluene diluent, g

194.556 = factor for converting g of cyclohexene per g of cyclohexene plus toluene diluent to bromine number, equal to the product:

$$\frac{(159.808)(100)}{82.14} \quad (1a)$$

where:

82.14 = the molecular weight of cyclohexene, g/mole

100 = conversion of g/g to g/100 g

159.808 = the molecular weight of bromine, g/mole

Calculate the theoretical bromine index to the nearest unit for the dilute Cyclohexene-Bromine Index reference standard solution using Equation 2:

$$\text{Theoretical Bromine Index} = R(1000) \frac{Y}{Z} \quad (2)$$

where:

Y = mass of Cyclohexene-Bromine Number reference standard solution, g

Z = mass of Cyclohexene-Bromine Number reference standard solution plus toluene diluent, g

R = Theoretical bromine number for the dilute Cyclohexene-Bromine Number reference standard solution as calculated in Equation 1.

1000 = conversion of grams to milligrams, mg/g

Verify the concentration of the potassium bromide-bromate standard solution by titrating one gram of Cyclohexene-Bromine Number reference standard solution as described under *Determination of Bromine Number*, or one gram of Cyclohexene-Bromine Index reference standard solution as described under *Determination of Bromine Index*. If the determined bromine number or bromine index is not within 3% of the calculated theoretical value for the reference solution (Equations 1 and 2), standardize the titrant using the procedure described in the *Appendix*.

Standardization of Titrant

The 0.5-N bromide-bromate solution is purchased as a certified standard. Alternatively, it may be prepared and standardized in the laboratory as described in the *Appendix*.

Prepare the 0.02-N bromide-bromate solution as described in *Reagents*. Calculate the normality of the nominally 0.02-N bromide-bromate solution using Equation 3:

$$\text{Normality of the nominally 0.02-N bromide-bromate solution} = 0.04U \quad (3)$$

where:

U = certified or standardized normality of the nominally 0.5-N bromide-bromate solution

0.04 = dilution factor, 40 mL / 1000 mL

Determination of Bromine Number

Since potentiometric recording titrators can vary, the exact settings are judgmental. Experience gained in the titration of Cyclohexene-Bromine Number reference standard solution (see *Standardization*) will provide guidance in the choice of settings that will produce an accurate value in a reasonable time. When the approximate bromine number is determined, a more appropriate sample size can be selected and the sample reanalyzed to obtain a precise result. Samples with bromine numbers less than 0.8 are analyzed by the bromine index procedure, while samples with bromine numbers greater than 24 are diluted prior to analysis (see Table 1).

Table 1

Sample Size for Expected Bromine Number

<u>Bromine Number</u>	<u>Sample Size, g</u>
0.8-3	4
3-6	2
6-12	1
12-24	0.5
24-120	Dilute 1 g in 10 g*
120-240	Dilute 0.25 g in 10 g*

* Dilutions are prepared in a glass vial in toluene. Weigh 1 g of the diluted sample into a titration beaker and titrate.

1. Pipet 100 mL of the bromine number titration solvent into the 250-mL titration beaker (see *Note 4*).
2. Flush a disposable syringe with needle and draw an aliquot of sample for analysis. Quickly remove any liquid adhering to the outside of the needle with a wiper and stopper the tip of the needle with a silicone rubber stopper.
 - The sample size needed is dependent on the expected bromine number. Use Table 1 as a guide in determining the sample amount needed.
3. Weigh the stoppered syringe plus sample to the nearest 0.1 mg.

4. Remove the silicone rubber stopper and inject the sample aliquot into the bromine number titration solvent
 - The needle tip is inserted directly above the level of the bromine index titration solvent to ensure that the entire sample dissolves in the solution and does not adhere to the cell walls.
5. Replace the stopper and reweigh the stoppered syringe to the nearest 0.1 mg. Calculate the mass of the sample injected by difference and record.
 - If an expected bromine number is not known, add approximately 1 g of sample to the titration cell and titrate. After an approximate bromine index is determined, a more appropriate sample size is selected and the sample is reanalyzed to obtain a precise result.
 - If, upon the addition of the sample to the titration solvent, or if, during the titration, the solution separates or becomes cloudy, then the sample size must be reduced by 50% and the titration repeated. Samples such as detergent alkylate are slow to react and must be analyzed accordingly.
6. Place a Teflon stir bar in the titration beaker and set it on the magnetic stirrer.
7. Insert the combination electrode and adjust the stirring speed to create a vortex in the solvent that does not develop bubbles at its center.
 - The adjustment of the stirring speed is *critical* for obtaining reproducible results on difficult to solubilize samples.
8. Allow the emf reading of the solution to stabilize prior to starting the titration. Operate the recording titrator according to the manufacturer's instructions over an emf range of 1.0 to -1.0 V with the 0.5-N bromide-bromate standard solution in the 10-mL buret. Set the operating parameters on the titrator to perform a potentiometric equivalence point titration at a titration rate of 0.1 mL/min, with a reduced rate of titrant addition in the vicinity of the endpoint, and the sensitivity to the equivalence point set to produce an accurate value.
9. The total volume of titrant added to reach the inflection point is used in the calculation. If the sample was diluted, appropriate blanks must be used.
10. Calculate the bromine number (see *Calculations*).

Determination of Bromine Index

Since potentiometric recording titrators can vary, the exact settings are judgmental. Experience gained in the titration of Cyclohexene-Bromine Index reference standard solution (see *Standardization*) will provide guidance in the choice of settings that will produce an accurate value in a reasonable time. When the approximate bromine index is determined, a more appropriate sample size can be selected and the sample reanalyzed to obtain a precise result. Samples with bromine indexes greater than 800 are analyzed by the bromine number procedure.

1. Pipet 100 mL of bromine index titration solvent into the 250-mL titration beaker (see *Note 3*).
2. Flush a disposable syringe with needle and draw an aliquot of sample for analysis. Quickly remove any liquid adhering to the outside of the needle with a wiper and stopper the tip of the needle with a silicone rubber stopper.
 - The sample size needed is dependent on the expected bromine index. Use Table 2 as a guide in determining the sample amount needed.
3. Weigh the stoppered syringe plus sample to the nearest 0.1 mg.
4. Remove the silicone rubber stopper and inject the sample aliquot into the bromine index titration solvent.
 - The needle tip is inserted directly above the level of the bromine index titration solvent to ensure that the entire sample dissolves in the solution and does not adhere to the cell walls.

5. Replace the stopper and reweigh the stoppered syringe to the nearest 0.1 mg. Calculate the mass of the sample injected by difference and record.
 - If an expected bromine index is not known, add approximately 1 g of sample to the titration cell and titrate. After an approximate bromine index is determined, a more appropriate sample size is selected and the sample is reanalyzed to obtain a precise result.
 - If, upon the addition of the sample to the titration solvent, or if, during the titration, the solution separates or becomes cloudy, then the sample size must be reduced by 50% and the titration repeated. Samples such as detergent alkylate are slow to react and must be analyzed accordingly.

Table 2**Sample Size for Expected Bromine Index**

<u>Bromine Index</u>	<u>Sample Sizes, g</u>
1-10	20-40
10-100	10-20
100-500	1
500-800	0.5

6. Place a Teflon stir bar in the titration beaker and set it on the magnetic stirrer.
7. Insert the combination electrode and adjust the stirring speed to create a vortex in the solvent that does not develop bubbles at its center.
 - The adjustment of the stirring speed is critical for obtaining reproducible results on difficult to solubilize samples.
8. Allow the emf reading of the solution to stabilize prior to starting the titration. Operate the titrator according to the manufacturer's instructions over an emf range of 1.0- to -1.0 V with the 0.02-N bromide-bromate standard solution in a 5-mL buret. Set the operating parameters on the titrator to perform a potentiometric equivalence point titration at a titration rate of 0.1 mL/min, with a reduced rate of titrant addition in the vicinity of the endpoint, and the sensitivity to the equivalence point set to produce an accurate value. Perform the titration using the conditions described.
 - Stable emf readings will not, however, be obtained when a slow reacting sample is titrated. This is demonstrated by a backward, positive mV drift of the titration curve and data. If no backward drifting is evident, the titration is satisfactory. If backward drifting has occurred, proceed as follows:
 Titrate at a rate of 0.1 mL/min, and either set the maximum allowable drift during the titration to 5 mV/min, in a one minute window, or adjust both the titration rate reduction in the vicinity of the equivalence point and the sensitivity to the equivalence point to maximum. The equivalence point is selected as the point at which the emf drift is zero or less than 5 mV/min.
9. The volume of the titrant added to reach the inflection point is used to calculate the bromine index (see *Calculations*).

Calculations

Calculate the bromine number for undiluted samples using Equation 4, and report to the nearest 0.1:

$$\text{Bromine Number} = \frac{7.9904(A - J)N}{W} \quad (4)$$

where:

A = volume of bromide-bromate solution used for titrating the sample, mL

J = average volume of bromide-bromate solution used for titrating the reagent blanks, mL

N = normality as generated bromine (Br₂) of bromide-bromate solution, eq/L
W = sample mass, g
7.9904 = factor for converting to g of bromine per 100 g of sample, equal to the product of:

$$\frac{(159.808)(100)}{(1000)(2)} \quad (4a)$$

where:

2 = equivalents per mole, eq/mol
100 = conversion of g/g to g/100 g
159.808 = the molecular weight of bromine, g/mole
1000 = conversion of mL to L, mL/L

If the sample was diluted, calculate the bromine number using Equation 5 and report to the nearest 0.1:

$$\text{Bromine Number} = \frac{7.9904(A - J)N}{\left(\frac{C}{D}\right)E} \quad (5)$$

where:

C = mass of sample diluted, g
D = mass of sample plus diluent, g
E = mass of diluted sample titrated, g
A, J, N, and 7.9904 = previously defined

Calculate the bromine index using Equation 6 and report to the nearest whole number:

$$\text{Bromine Index} = \frac{7990.4(F - G)S}{V} \quad (6)$$

where:

F = volume of bromide-bromate solution used for titrating the sample, mL
G = average volume of bromide-bromate solution used for titrating the reagent blanks, mL
V = sample mass, g
S = normality as generated bromine (Br₂) of bromide-bromate solution, mol/L
7990.4 = factor for converting to milligrams of bromine per 100 g of sample, equal to the product of:

$$\frac{(159.808)(100)(1000)}{1000(2)} \quad (6a)$$

where:

2 = equivalents per mole, eq/mol
100 = conversion of mg/g to mg/100 g
159.808 = molecular weight of bromine, g/mole
1000 = in the numerator, conversion of grams to milligrams, mg/g
1000 = in the denominator, conversion of mL to L, mL/L

Notes

1. A classical two-electrode system may be used instead of the single combination platinum electrode specified herein. However, the resulting titration curve may contain noise and be difficult to interpret. Acceptable electrodes for the classical system are: a glass reference

electrode, Metrohm USA, Cat. No. 020911000, and a platinum indicating electrode, Metrohm USA, Cat. No. 020924306.

2. A stabilizer, often an olefin, added to methylene chloride, prevents decomposition of the methylene chloride. A possible decomposition product of unstabilized methylene chloride is phosgene and, therefore, a minimum quantity should be maintained in the laboratory.
3. Occasionally a precipitate will form in the bottom of the bromine index titration solvent. The precipitate should be left in contact with the titration solvent. Do not transfer any precipitate to the titration beaker.
4. The procedure may be automated through the use of an autosampler.

Precision

Precision statements were determined using UOP Method 999.

Repeatability and Site Precision

A nested design was carried out for determining the bromine index of two samples and the bromine number of two samples with two analysts in one laboratory. Each analyst carried out two tests on two separate days, performing two tests on each sample each day. The total number of tests was 32. The precision data are summarized in Table 1. Two tests performed by the same analyst on the same day should not differ by more than the repeatability allowable difference with 95% confidence. Two tests performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable difference with 95% confidence.

The data in Table 1 are a short-term estimate of repeatability. When the test is run routinely, a control standard and chart should be used to develop a better estimate of the long-term repeatability.

Table 1

Repeatability and Site Precision

	<u>Mean</u>	<u>Repeatability</u>		<u>Site Precision</u>	
		<u>Within-Day esd</u>	<u>Allowable Difference</u>	<u>Within-Lab esd</u>	<u>Allowable Difference</u>
Bromine Index	14.8	0.43	1.7	0.50	2.0
Bromine Index	101.0	1.60	6.3	1.94	7.6
Bromine Number	1.9	0.03	0.1	0.04	0.2
Bromine Number	14.7	0.18	0.7	0.21	0.8

Reproducibility

There is insufficient data to calculate reproducibility of the test at this time.

Bias

Since bromine number and bromine index are defined in terms of a method, there is no bias.

Time for Analysis

The elapsed time for one analysis can vary from 0.5 to 2 hours. The labor requirement is 0.25 hour.

Suggested Suppliers

Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219-4785 (412-490-8300) www.fishersci.com

LabChem Inc., 200 William Pitt Way, Pittsburgh, PA 15238 (412-826-5230) www.labchem.net

National Institute of Standards and Technology (NIST), Standard Reference Materials Group, 100
Bureau Dr., Gaithersburg, MD 20899 (301-975-6776) www.nist.gov

Metrohm USA, 6555 Pelican Creek Circle, Riverview, FL 33578 (813-316-4700)
www.metrohmusa.com

VWR International, 1310 Goshen Parkway, West Chester, PA 19380 (610-431-1700) www.vwr.com

Wilmad/Lab-Glass, 1002 Harding Hwy., Buena, NJ 08310 (856-697-3000) www.wilmad-labglass.com

Appendix

Preparation and Standardization of Bromide-Bromate Solution

Scope

This appendix describes the preparation and standardization of the 0.5-*N* bromide-bromate solution if it is prepared in the laboratory and not purchased as a certified solution. See *Reagents* in the body of the method.

It is also used to check the standardization of the bromide-bromate solution if the determined bromine number or bromine index of either of the cyclohexene reference solutions do not agree within 3% of their theoretical value. See *Standardization* under *Procedure* in the body of the method.

Apparatus

The following apparatus are required in addition to the apparatus listed in the body of the method.

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Cylinder, graduated, Class B, 10-mL, VWR, Cat. No. 89001-110

Dish, evaporating, 50-mL, VWR, Cat. No. 25313-050

Flask, iodine determination, 500-mL, with stopper, VWR, Cat. No. 89001-840

Oven, capable of operation at 110°C

Pipets, volumetric transfer, Class A, 5-mL, VWR, Cat. No. 89002-768

Stopwatch/Timer, digital, VWR, Cat. No. 61161-308

Reagents

The following reagents are required in addition to the reagents listed in the body of the method.

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used. References to water mean double-deionized or triple-distilled water.

Hydrochloric acid solution, 1-*N* (1-*M*), VWR, Cat. No. VW3202-1

Ice

Potassium bromate, 99.8% minimum purity, VWR, Cat. No. EM-PX1374-2

Potassium dichromate, primary standard, NIST, Cat. No. SRM 136e. Oven dry at 100°C for 2 hours.

Potassium iodide, granular, 99.0% minimum purity, VWR, Cat. No. EM-PX1507-1

Potassium iodide, 15% solution. Dissolve 15 g $\pm$ 0.01 g of potassium iodide in 80 mL of water in a 100-mL volumetric flask. Dilute to the mark with water and mix well.

Sodium thiosulfate solution, 0.1-*N* (0.1-*M*), VWR, Cat. No. VW3228-1

Sodium thiosulfate solution, 0.01-*N*. Pipet 100 mL of standardized 0.1-*N* sodium thiosulfate solution into a 1000-mL volumetric flask. Fill to the mark with water and mix well. Make up fresh daily or when needed.

Starch indicator solution, stabilized, Fisher Scientific, Cat. No. SS408-1

Procedure

Preparation of 0.5-N Bromide-Bromate Standard Solution

Prepare the nominally 0.5-N bromide-bromate solution as follows:

1. Dry approximately 20 g of potassium bromate in an oven for 30 minutes.
2. Using a graduated cylinder, add 500 mL of water to a 1000-mL volumetric flask.
3. Weigh $13.920 \text{ g} \pm 0.001 \text{ g}$ of the dried potassium bromate and add it to the flask.
4. Weigh $51.0 \pm 0.01 \text{ g}$ of potassium bromide and add it to the flask.
5. Fill to the mark with water and mix well.

Standardization of Titrant

This is required only if the 0.5-N bromide-bromate titrant is made in the laboratory and not purchased as a certified solution, or if the certification of the solution needs to be checked.

Standardize the 0.1-N sodium thiosulfate as follows:

1. Weigh approximately 0.2 g, to the nearest 0.1 mg, of potassium dichromate into a glass-stoppered 500-mL iodine determination flask.
2. With a graduated cylinder, add 67 mL of water and 13 mL of potassium iodide solution to the flask. Mix well to dissolve the dichromate.
3. While swirling, add 20 mL of 1-N hydrochloric acid to the flask, stopper and place the flask in the dark for 10 minutes.
4. Titrate the dichromate solution potentiometrically with 0.1-N sodium thiosulfate using the platinum combination electrode. Add one milliliter of starch indicator solution to assist with the determination of the end point (disappearance of the blue color).
 - The addition of the starch solution is not mandatory, but may assist in the identification of the endpoint.

Calculate the molarity of the 0.1-N sodium thiosulfate solution using Equation A1:

$$K = 20.3950 \frac{L}{Q} \quad (\text{A1})$$

where:

K = molarity of 0.1-N sodium thiosulfate, mol/L

L = mass of potassium dichromate, g

Q = volume of 0.1-N sodium thiosulfate used to titrate potassium dichromate, mL

20.3950 = factor for converting g of potassium dichromate per mL of sodium thiosulfate to molarity, equal to the product:

$$\frac{(1000)(6)}{294.19} \quad (\text{A1a})$$

where:

6 = number of electrons transferred during redox titration of potassium dichromate

294.19 = molecular weight of potassium dichromate, g/mole

1000 = conversion of mL to L

Calculate the molarity of the 0.01-*N* sodium thiosulfate using Equation A2:

$$P = K(0.10) \quad (A2)$$

where:

K = as previously calculated, Equation 1

P = molarity of 0.01-*N* sodium thiosulfate, mol/L

0.10 = factor incorporating the volume of 0.1-*N* sodium thiosulfate pipeted and the volume to which it was diluted, **100 / 1000**

Standardize the 0.5-*N* bromide-bromate titrant as follows:

1. Add 50 mL of glacial acetic acid and 1 mL of hydrochloric acid to a glass stoppered, 500-mL iodine determination flask. Stopper and chill in a wet ice bath for approximately 10 minutes.
2. Pipet 5 mL of the bromide-bromate titrant into the iodine flask dropwise at a rate of 1 to 2 drops per second while swirling the flask. Immediately stopper the flask and shake vigorously. Return the flask to the wet ice bath.
3. With a graduated cylinder, place 5 mL of potassium iodide solution in the lip of the flask. After 5 minutes, remove the flask from the ice bath. Slowly remove the glass stopper allowing the potassium iodide to drain from the lip into the flask and immediately shake vigorously.
4. Add 100 mL of water, rinsing the stopper and the flask lip and walls.
5. Immediately titrate potentiometrically with the 0.1-*N* sodium thiosulfate. Add 1 mL of starch solution to assist with the end point determination (the blue color disappears).

Calculate the normality of the 0.5-*N* bromide-bromate solution using Equation A3:

$$H = \frac{SP}{T} \quad (A3)$$

where:

H = normality as generated bromine (Br₂) of 0.5-*N* (0.25-*M*) bromide-bromate solution, eq/L

P = as previously calculated, Equation A1

S = volume of 0.01-*N* sodium thiosulfate solution used for the titration of the bromide-bromate solution, mL

T = volume of 0.5-*N* bromide-bromate solution titrated, mL

Use this value as *N* in Equation 4 in the body of the method.