

ALKALINITY, SULFIDE AND MERCAPTIDE ANALYSES OF USED REFINERY CAUSTIC SOLUTIONS

UOP Method 209-00

SCOPE

This method is for the analysis of used refinery caustic solutions. Part A is for determining the strong base, weak base (spent caustic) and total alkalinity. Part B is for determining the concentration of sulfur present as sodium sulfide and sodium mercaptide. The data generated using this method are considered quantitative over the concentration ranges generally encountered in these types of refinery caustic solutions. Refinery caustic samples are inherently unstable, and must be analyzed as soon as possible after they are drawn.

Part A, a potentiometric titration, is an accurate procedure for use in distinguishing between strong bases, i.e., sodium phenolate and sodium hydroxide. The *APPENDIX* contains a procedure, *Caustic Solution Analysis - Double Indicator*, which can be used as a convenient, although not rigorous, test for the plant control of refinery caustic solutions used to remove hydrogen sulfide, mercaptans and certain other weak acids from petroleum products.

OUTLINE OF METHOD

Part A - Determination of Alkalinity of Used Refinery Caustic Solutions

The strong bases, weak bases, and total alkalinity are determined by titrating with standard acid using a potentiometric procedure. The titration of the strong bases to an endpoint in a pH range from 9 to 6 includes sodium hydroxide, the first endpoint of sodium carbonate, the first endpoint of sodium sulfide, sodium alkyl mercaptides and sodium phenolates (see Note 1). The titration of the weak bases, from a pH of about 6 to an endpoint in a pH range from 4 to 3, includes sodium bicarbonate, sodium bisulfide, sodium naphthenates and sodium thiophenolates (sodium aryl mercaptides), see Note 2. The salts of strong acids, such as sodium chloride, sodium sulfate, sodium thiosulfate and sodium alkane sulfonates, are not basic and do not titrate (see Note 7).

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

Part B - Determination of Mercaptide and Sulfide in Caustic Solutions

The sample is dissolved in a titration solvent containing equal volumes of 2-propanol and aqueous sodium hydroxide, with 1% by volume of concentrated ammonium hydroxide. The solution is titrated potentiometrically with standard alcoholic silver nitrate using a combination glass/silver electrode. The concentration of sulfur present as sodium sulfide and sodium mercaptide is calculated as mass-% sulfur. Caustic solutions containing high levels of mercaptide and low levels of sulfide are titrated separately for the two components. A sample is titrated to the mercaptide endpoint, and a larger sample is titrated only to the sulfide endpoint. The mercaptide concentration is determined by difference. If the ratio of sulfide sulfur to mercaptide sulfur is greater than 10:1, then the mercaptide result is considered to be qualitative.

DEFINITIONS

Strong Base

1. When only one break in the titration curve is present in the pH range from 9 to 6, this break will be considered the endpoint of all strong bases present (see Fig. 2, Curve A).
2. When two breaks are present in the titration curve, the first break will be considered the endpoint of all the strong bases present (see Fig. 2, Curve C and Fig. 3, Curves A and B).
3. When three breaks are present in the titration curve, the second break will be considered the endpoint of all the strong bases present (see Fig. 1, Break B; Fig. 2, Curves B and D; and Fig. 3, Curve C).

Weak Bases

1. When only two breaks are present, the second break in the titration curve will be considered the endpoint of all the weak bases present (see Fig. 2, Curve C and Fig. 3, Curves A and B).
2. When three breaks are present, the third break in the titration curve will be considered the endpoint of all the weak bases present (see Fig. 1, Break C; Fig. 2, Curves B and D; and Fig. 3, Curve C).

Total Alkalinity

1. When only two breaks are present, the second break in the titration curve will be considered the endpoint of all the bases present (see Fig. 2, Curve C and Fig. 3, Curves A and B).
2. When three breaks are present, the third break in the titration curve will be considered the endpoint of all bases present (see Fig. 1, Break C; Fig. 2, Curves B and D; and Fig. 3, Curve C).

Percent Spent

The expression “% Spent” is an approximate but useful measure of the condition of a refinery caustic used to remove weak acids.

$$\% \text{ Spent} = 100 \frac{(\text{Weak Base})}{(\text{Total Base})} \quad (1)$$

or

$$\% \text{ Spent} = 100 \frac{(\text{Total Base}) - (\text{Strong Base})}{(\text{Total Base})} \quad (2)$$

APPARATUS

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

Balance, capacity 200 g, readability ± 0.1 -mg

Beaker, electrolytic, tall form, 300-mL, Fisher Scientific, Cat. No. 10-310-8

Cylinder, graduated, Class B, 100-mL, Fisher Scientific, Cat. No. 08-549-5E

Desiccator, Fisher Scientific, Cat. No. 08-631A

Electrode, combination glass, pH 0-14, Brinkmann Instruments, Cat. No. 20-91-050-0 (see Note 8)

Electrode, combination glass/silver Titrode, Brinkmann Instruments, Cat. No. 20-94-850-7. The electrode should be dedicated to sulfur analysis.

Flask, Erlenmeyer, 500-mL, Fisher Scientific, Cat. No. 10-040H

Flasks, volumetric, Class A, 250- and 500-mL, Fisher Scientific, Cat. Nos. 10-211E and -211F, respectively

Oven, drying, suitable for operation at 110°C

Pipets, volumetric, Class A, 5-, 10-, 25- and 50-mL, Fisher Scientific, Cat. Nos. 13-650-2F, -2L, -2P and -2S, respectively

Regulator, nitrogen, two-stage, high purity, Matheson Gas Products, Cat. No. 3122-580

Scotchbrite™ abrasive cleaning pads, or equivalent, local supply

Stirring bars, magnetic, Teflon™-covered, Fisher Scientific, Cat. No. 14-511-94

Titration, potentiometric, recording, ± 2000 -mV range, 1-mV resolution with a dispenser having a volume readout of 0.00 to 20.00 mL and 0.01% resolution, Brinkmann Instruments, Cat. No. 20-87-254-3

REAGENTS AND MATERIALS

All reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, when such specifications exist, unless otherwise specified. References to water mean deionized or distilled water. Unqualified references to solutions mean aqueous solutions.

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

Ammonium hydroxide, concentrated, Fisher Scientific, Cat. No. A669-212

Buffer solutions, pH 4, 7 and 10, color-coded, Fisher Scientific, Cat. Nos. SB101-500, SB107-500 and SB115-500, respectively

Drierite desiccant, indicating, Fisher Scientific, Cat. No. 07-578-3A

Hydrochloric acid, 0.1-*M*, standardized to 0.0001, Fisher Scientific, Cat. No. SA54-1

Nitrogen, cylinder, 99.9% minimum purity

Paper, test, lead acetate, vial, Fisher Scientific, Cat. No. 14-862

2-Propanol, oxygen free, Fisher Scientific, Cat. No. A416-4. Purge the contents of a freshly-opened bottle with nitrogen for one hour and store under nitrogen.

Silver nitrate, alcoholic, 0.01-*M*, standardized to 0.0001, Fisher Scientific, Cat. No. LC22745-2

Sodium hydroxide, approximately 1-*M* and 5-*M*, stripped with nitrogen, Fisher Scientific, Cat. Nos. SS266-1 and SS256-500, respectively

Sodium sulfide, 9-hydrate, Fisher Scientific, Cat. No. S425-500

Sodium sulfide, 1% solution. Dissolve 1.0 ± 1.0 mg of sodium sulfide in 100 mL of water.

THAM, tris(hydroxymethyl)aminomethane, alkalimetric standard, Fisher Scientific, Cat. No. T395. Dry in an oven at 110°C for 2 hours before using. Cool in a desiccator.

Titration solvent, oxygen free, equal volumes of nitrogen-purged 2-propanol and 1-*M* sodium hydroxide. Add 1% by volume of concentrated ammonium hydroxide. Store under nitrogen.

PROCEDURE

Silver–Silver Sulfide Electrode Preparation and Reconditioning

Proper electrode preparation is essential to obtain reproducible and noise-free titration curves having good endpoints. The electrode should be reconditioned on a weekly basis when in use, and must be reconditioned if it is used for any titrations other than sulfur compounds. An electrode should be dedicated to sulfur analysis. Prepare and recondition the silver-silver sulfide electrode as follows:

1. Clean the silver surface with a Scotchbrite™ pad. Rinse with water and dry.
2. Immerse the electrodes in a solution containing 90 mL of 2-propanol, 2 mL of ammonium hydroxide and 8 mL of 1% sodium sulfide solution.
3. Slowly add approximately 10 mL of 0.01-*N* silver nitrate solution over a period of 10 minutes while stirring at a moderate speed. A film of silver sulfide will be deposited on the silver electrode.

4. Wipe the excess silver sulfide from the electrode with a soft paper towel.
 - The electrode should be cleaned after each titration by rinsing with water.

Standardization

1. Weigh approximately 0.1 g of previously dried THAM, to the nearest 0.1 mg, into each of two clean, dry titration beakers.
2. Add a magnetic stirring bar and approximately 100 mL of deionized water to each beaker.
3. Titrate the contents of both beakers with 0.1-*M* hydrochloric acid using the automated titrator, with combination glass electrode, according to the manufacturer's directions.
4. Record the volume of titrant required to reach the endpoint of each titration.
5. Calculate the molarity of the hydrochloric acid to the fourth decimal place for both titrations as follows:

$$M_1 = \frac{1000 W}{121.14 V} \quad (3)$$

where:

M₁ = molarity of hydrochloric acid, mol/L

V = volume of hydrochloric acid required to reach the endpoint, mL

W = mass of THAM weighed into beaker, g

121.14 = molecular weight of THAM, g/mol

1000 = factor to convert L to mL

- The duplicates should agree within 0.001 mol/L. If not, redry the THAM or check the equipment and repair as necessary. Then rerun the standardization until the guideline is met.
6. Record the average molarity of the hydrochloric acid for use in *CALCULATIONS*.

Part A - Determination of Alkalinity of Used Refinery Caustic Solutions

1. Prepare the automatic titrator using the combination glass electrode according to the manufacturer's directions (see Note 8). Calibrate with pH standard buffers.
2. Pipet 10 mL of the sample of used caustic solution into a tared 500-mL volumetric flask. Weigh the flask containing the sample, calculate and record the sample mass.
 - Some caustic samples have a hydrocarbon layer floating on the surface. The caustic sample taken for analysis must not contain any of this hydrocarbon layer.
3. Dilute to the mark with water and thoroughly mix the contents of the flask.
4. Pipet an aliquot of the diluted sample that will yield a titration of 5 to 15 mL into a 250-mL electrolytic titration beaker. Add approximately 100 mL of water and a magnetic stirring bar.
5. Titrate with 0.1-*M* hydrochloric acid using the combination glass electrode.
 - Samples should be titrated immediately after dilution to prevent loss of basic sulfur compounds by oxidation.

- More than one inflection may be observed in the titration curve. The endpoint for any one inflection is taken where $\Delta\text{pH} / \Delta\text{mL}$ is a maximum, i.e., where the change in pH per unit of titrant added is the greatest. The first break at a pH in the range of 9 to 6 represents the strong bases. The break at a pH in the range of 4 to 3 represents the weak bases (see Figs. 1, 2 and 3). Calculate the strong base using the break at the higher pH value as the endpoint. Calculate the total alkalinity using the break at the lower pH value as the endpoint. The weak base (spent caustic), as previously defined, is the difference between the total alkalinity and the strong bases present.

Part B - Determination of Mercaptide and Sulfide in Caustic Solutions

1. Prepare the automatic titrator using the combination glass/silver Titrode according to manufacturer's directions.
 - The electrode should be conditioned according to the procedure in *Electrode Preparation*.
2. Weigh a portion of the original caustic sample, to the nearest 0.1 mg, into a 250-mL electrolytic beaker. Use Table 1 as a guide in selecting the proper sample size.
 - The sample size should be selected according to Table 1 to give a titration of at least 2 mL.
 - Some caustic samples have a hydrocarbon layer floating on the surface. The caustic sample weighed for analysis must not contain any of this hydrocarbon layer.
3. Add approximately 100 mL of the titration solvent to the sample and titrate with 0.01-M alcoholic silver nitrate.
 - Caustic containing sulfide and mercaptide should be titrated so that a minimum amount of oxygen comes in contact with the caustic. Provide a nitrogen blanket over the titration beaker while titrating. Do not bubble nitrogen through the caustic solution because this would result in stripping out hydrogen sulfide, mercaptan and ammonia.
 - The titrator should be programmed to add the titrant at a rate not to exceed 0.1 mL/min as the endpoint is approached.

If both sulfide and mercaptide ions are present, two inflections will be noted in the titration curve (see Fig. 4). If only one inflection is present, confirm the identity of the species present with lead acetate test paper. Moisten a piece of lead acetate test paper with water and add one drop of the caustic. If the paper turns silver-black, the test is positive and sulfide ion is present in the sample. Some mercaptides will cause lead acetate paper to darken with a tan to yellow coloration; this is not to be confused with a positive sulfide test.

Table 1
Suggested Sample Size

<u>Expected NaSR and Na₂S Content, mass-%</u>	<u>Suggested Sample Mass, g</u>
< 0.02	10
0.02 – 0.05	5
0.05 – 0.10	1
0.10 – 0.50	0.3
> 0.50	0.1

Titration of Sulfide in the Presence of High Concentrations of Mercaptide

Caustic used to extract sulfur compounds can be quite high in mercaptide. If sodium sulfide is present in small concentrations, the high mercaptide content will have the effect of masking the sulfide break. It is, therefore, necessary to titrate separately for the sulfide and mercaptide.

1. Weigh a sample sufficiently large so that the sulfide break can be discerned, if sulfide is present.
2. Titrate the sample according to Steps 1 through 3 in *Part B - Determination of Mercaptide and Sulfide in Caustic Solutions*.
3. Discontinue the titration after the sulfide break is complete.
4. Titrate a smaller sample portion for mercaptide analysis to the mercaptide break according to the same procedure.

CALCULATIONS

All results from calculations should be rounded to no more than two significant figures for reporting purposes.

Part A - Determination of Alkalinity of Used Refinery Caustic Solutions

$$\text{Total Alkalinity, as NaOH, mass - \%} = \frac{4.00 \text{ AM}_1\text{P}}{\text{WR}} \quad (4)$$

where:

A = total volume of acid used to reach potentiometric endpoint at pH of about 3.5, mL

M₁ = molarity of acid used, mol/L

P = volume to which the sample is originally diluted, mL

R = volume of the aliquot taken for measurement, mL

W = mass of sample, g

4.00 = [(molecular weight of NaOH, 40.0 g/mol)(100%)] / (1000 mL/L)

$$\text{Strong Base, as NaOH, mass - \%} = \frac{4.00 \text{ BM}_1\text{P}}{\text{WR}} \quad (5)$$

where:

B = volume of acid used to reach potentiometric endpoint at pH of about 9, mL

M₁, P, R, W and 4.00 = previously defined, Eq. 4

$$\text{Spent (weak) base, as NaOH, mass - \%} = 100 \frac{(a - b)}{a} \quad (6)$$

where:

a = total alkalinity, mass-%, as calculated in Eq. 4

b = strong base, mass-%, as calculated in Eq. 5

Part B - Determination of Mercaptide and Sulfide in Caustic Solutions

$$\text{Sulfide Sulfur, mass - \%} = \frac{1.60 E M_2}{W_1} \quad (7)$$

where:

E = volume of silver nitrate used to reach the sulfide ion endpoint, mL

M₂ = molarity of silver nitrate solution, mol/L

W₁ = mass of sample, g

1.60 = [(atomic weight of sulfur, 32.066 g/mol)(100%)] / [(2 mol silver nitrate/mol sulfur) (1000 mL/L)]

$$\text{Mercaptide Sulfur, mass - \%} = \frac{3.21 (D - E) M_2}{W_1} \quad (8)$$

where:

D = total volume of silver nitrate used to reach mercaptide ion endpoint, mL

E, M₂ and W₁ = previously defined, Eq. 7

3.21 = [(atomic weight of sulfur, 32.066 g/mol)(100%)] / (1000 mL/L)

When sulfide is very low and mercaptide is high:

$$\text{Sulfide Sulfur, mass - \%} = \frac{1.60 E M_2}{W_2} \quad (9)$$

where:

E, M₂ and 1.60 = previously defined, Eq. 7

W₂ = mass of large sample taken to obtain only the sulfide break, g

$$\text{Mercaptide Sulfur, mass - \%} = \frac{3.21 D M_2}{W_3} - 2C \quad (10)$$

where:

C = sulfide sulfur, mass-%, Eq. 9

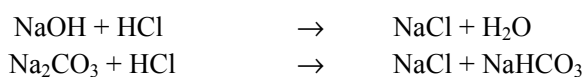
D and 3.21 = previously defined, Eq. 8

M₂ = previously defined, Eq. 7

W₃ = mass of sample taken to obtain only the mercaptide break, g

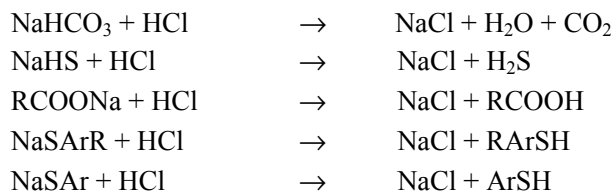
NOTES AND PRECAUTIONS

- Typical reactions for strong bases:





2. Typical reactions for weak bases:



3. Caustic solutions that contain sulfur compounds are quite susceptible to oxidation in air. The samples should, therefore, be protected by blanketing with an inert gas such as nitrogen.
4. If it is necessary to dilute the sample in a volumetric flask for the sulfide or mercaptide determination, dilute with nitrogen-stripped 5-M sodium hydroxide instead of water. This will prevent oxidation hydrolysis and, therefore, loss of mercaptides and sulfides.
5. If the titrator is programmed to be too sensitive, it is possible to obtain multiple endpoints along the titration curve. It is best to use an automated titrator capable of displaying the first derivative of the titration curve to determine the proper endpoint(s) in this case.
6. Samples containing high levels of sulfide and low levels of mercaptide will not provide a quantitative result for mercaptide if the ratio of sulfide sulfur to mercaptide sulfur is greater than 10:1.
7. An estimate of the non-titratable sodium salts, such as sodium chloride, sodium sulfate, sodium thiosulfate and sodium alkane sulfonates, in the used refinery caustic solution can be obtained by subtracting the total base concentration (strong bases plus weak bases), Part A, from the base concentration indicated by the specific gravity. The specific gravity and subsequent base concentration as weight-% sodium hydroxide are obtained as indicated in the *APPENDIX*.
8. A separate glass and silver chloride reference electrode may be substituted for the combination electrode.

PRECISION

Due to the inherent instability of these types of refinery caustic samples, the precision data captured in Table 2 were collected within a single working day. The precision statements were developed using UOP Method 999.

ASTM Repeatability

A nested design was carried out for strong bases, weak bases, sulfide and mercaptide analysis (using both Parts A and B of the method) in refinery caustic with two analysts. Each analyst carried out tests on a single day, performing eight tests each on a single sample. The total number of tests performed was 16. Using a stepwise analysis of variance procedure, the within-day estimated standard deviations (esd) were calculated for basicity, sulfide and mercaptide and are listed in Table 2. Two tests performed by the same

analyst on the same day should not differ by more than the ASTM allowable differences shown in Table 2 with 95% confidence.

UOP Repeatability

A nested design was carried out for strong bases, weak bases, sulfide and mercaptide analysis (using both Parts A and B of the method) in a refinery caustic with two analysts. Each analyst carried out tests on a single day, performing eight tests each on a single sample. The total number of tests performed was 16. Using a stepwise analysis of variance procedure, the within-lab estimated standard deviations (esd) were calculated for basicity, sulfide and mercaptide and are listed in Table 2. Two tests performed in one laboratory by different analysts on the same day should not differ by more than the UOP allowable differences shown in Table 2 with 95% confidence.

Table 2
ASTM and UOP Repeatability, mass-%

Component	Mean	ASTM Repeatability		UOP Repeatability	
		Within-Day esd	Allowable Difference	Within-Lab esd	Allowable Difference
Strong Bases	5.2	0.06	0.2	0.07	0.2
Weak Bases	7.2	0.05	0.2	0.06	0.2
Sulfide	0.87	0.013	0.04	0.021	0.08
Mercaptide	1.1	0.04	0.1	0.05	0.2

Reproducibility

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

TIME FOR ANALYSIS

The elapsed time and labor requirements for one analysis are identical, one hour.

REFERENCE

UOP Method 999, "Precision Statements in UOP Methods"

SUGGESTED SUPPLIERS

Brinkmann Instruments, Inc., One Cantiague Rd., P.O. Box 1019, Westbury, NY 11590-0207 (516-334-7500)

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

Matheson Gas Products, P.O. Box 96, Joliet, IL 60434 (815-727-4848)

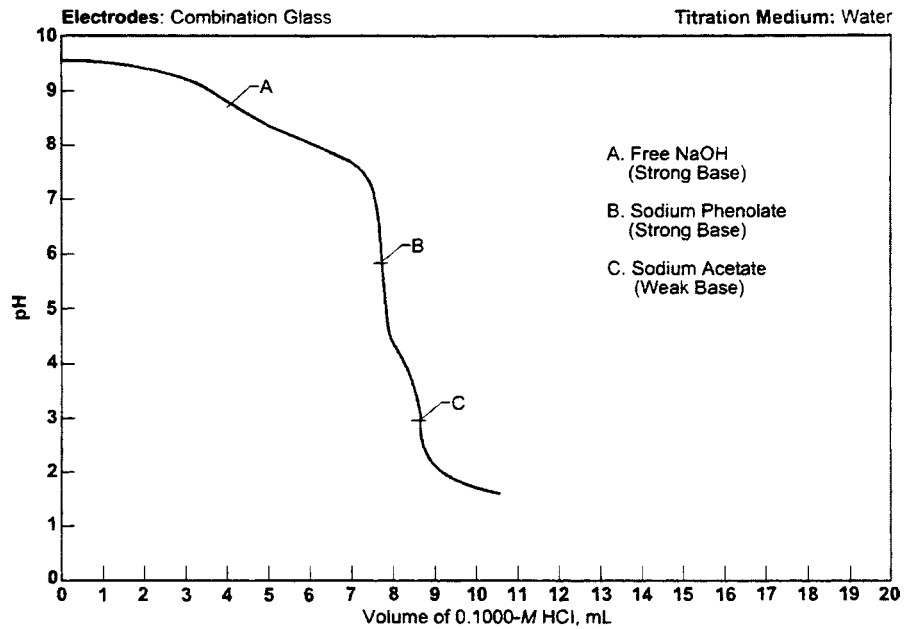


Figure 1

Potentiometric Titration of Synthetic Refinery Caustic for Basicity

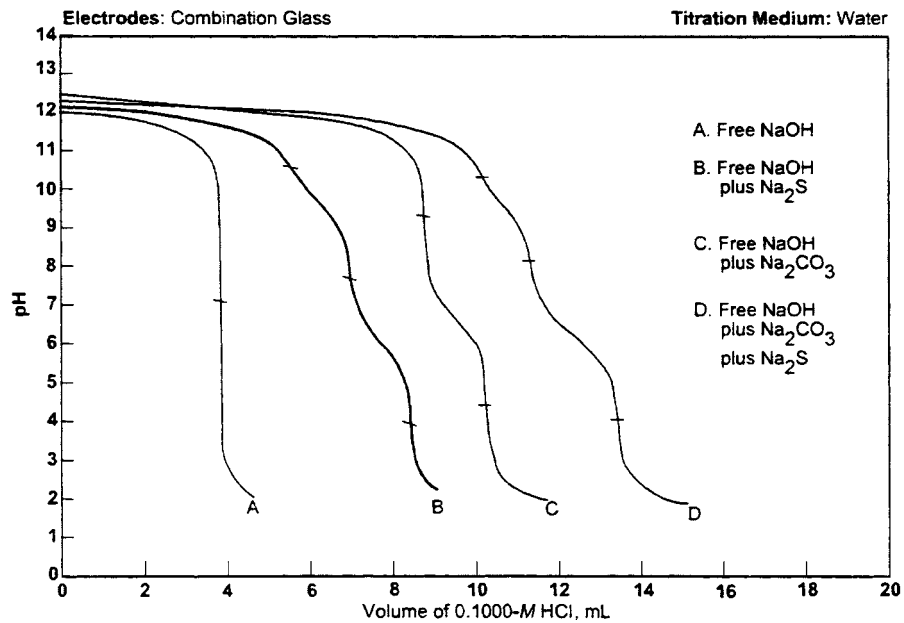


Figure 2

Potentiometric Titration of Synthetic Refinery Caustic for Basicity

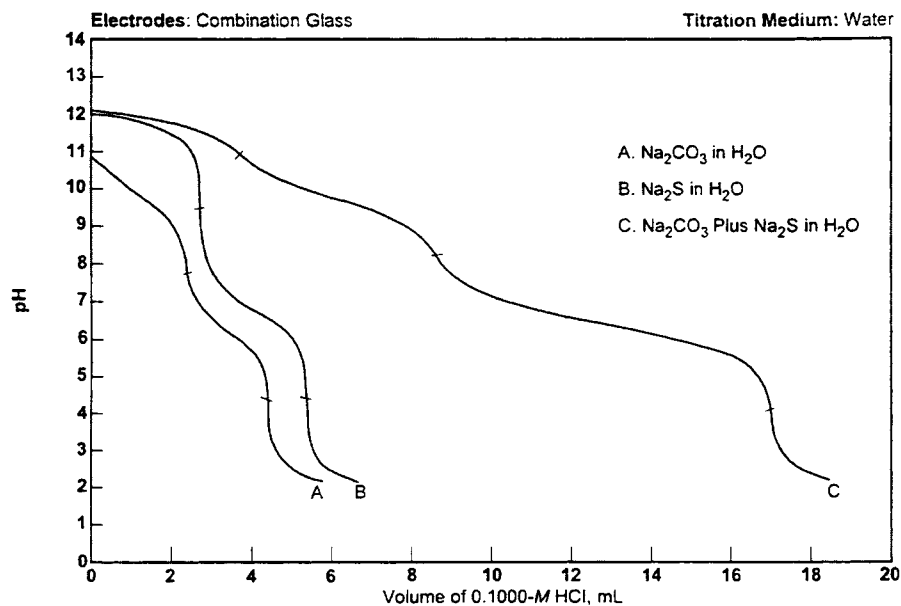


Figure 3

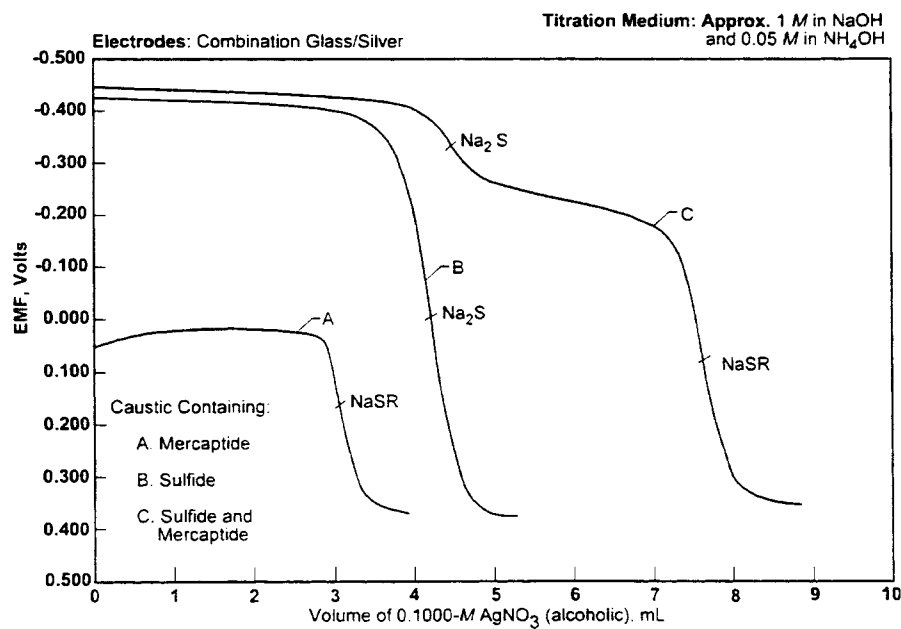
Potentiometric Titration of a Mixture of Na_2S and Na_2CO_3 

Figure 4

Potentiometric Titration of Mercaptides and Sulfides in Refinery Caustics

APPENDIX

Caustic Solution Analysis - Double Indicator

SCOPE

This appendix is a convenient, though not rigorous, test for the plant control of refinery caustic solutions used to remove hydrogen sulfide, mercaptans and certain other weak acids from petroleum products. The method is also applicable to Merox[®] circulating caustic. The results are significant only when correlated with plant experience.

OUTLINE OF METHOD

This method uses two indicators to distinguish strong bases from weak bases present in the sample. Strong bases in the sample are titrated with standard acid to the bromothymol blue endpoint. Strong plus weak bases in the sample are titrated with standard acid to the bromophenol blue endpoint to determine total alkalinity.

The titration of the strong bases to the bromothymol blue endpoint includes sodium hydroxide, sodium alkyl mercaptides, sodium phenolates and the first endpoint of sodium carbonate and sodium sulfide (see Method, *Notes and Precautions 1*).

The titration of a second sample of the caustic to the bromophenol blue endpoint is used to estimate the total alkalinity. This includes all of the strong bases included in the first titration plus the following weak bases: sodium bicarbonate, sodium bisulfide, sodium naphthenates and sodium thiophenolates (sodium aryl mercaptides), see Method, Note 2. Sodium thiosulfate interferes with the bromophenol blue endpoint in that the color at endpoint slowly fades. However, this is not a serious drawback since this method is an approximate procedure. The salts of strong acids, such as sodium chloride, sodium sulfate, sodium thiosulfate and sodium alkane sulfonates, are not basic and do not titrate, see *NOTE*.

APPARATUS

The following apparatus is required in addition to the apparatus listed in the main method.

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

Buret, Class A, 50- and 100-mL, Fisher Scientific, Cat. Nos. 03-701-25C and -25D, respectively

Cylinder, graduated, Class B, 50-mL, Fisher Scientific, Cat. No. 08-549-5D

Flask, Erlenmeyer, 250-mL, Fisher Scientific, Cat. No. 10-040F, several required

Hydrometer, specific gravity and Baume scales, heavy liquids, 300-mm, double scales, specific gravity range from 1.000 to 1.220 in subdivisions of 0.002 and Baume range from 0° to 26° in subdivisions of 0.2°, Fisher Scientific, Cat. No. 11-540A

REAGENTS AND MATERIALS

The following reagents and materials are required in addition to those listed in the main method.

All reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, when such specifications exist, unless otherwise specified. References to water mean deionized or distilled water. Unqualified references to solutions mean aqueous solutions.

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

Bromophenol blue, Fisher Scientific, Cat. No. B392-5

Bromophenol blue indicator solution. Dissolve 0.1 ± 0.001 g of bromophenol blue in 7.5 mL of 0.02-*M* sodium hydroxide and dilute with water to 250 mL. Cap and invert several times to thoroughly mix.

Bromothymol blue, Fisher Scientific, Cat. No. B388-10

Bromothymol blue indicator solution. Dissolve 0.1 ± 0.001 g of bromothymol blue in 7.5 mL of 0.02-*M* sodium hydroxide and dilute with water to 250 mL. Cap and invert several times to thoroughly mix.

Hydrochloric acid, aqueous, 0.100-*M*, standardized, Fisher Scientific, Cat. No. SA54-1

2-Propanol, Fisher Scientific, Cat. No. A416-4

Sodium hydroxide solution, 0.02-*M*, Fisher Scientific, Cat. No. SS282-1

PROCEDURE

1. Obtain a sample of the caustic solution and determine the specific gravity at room temperature by means of the appropriate hydrometer, see ASTM Method D 1298. Refer to any appropriate published table, such as that found in the *CRC Handbook of Chemistry and Physics*, to convert the specific gravity of the sample to the approximate total alkalinity as weight-% sodium hydroxide.
 - This information is used to determine the suggested sample size, see *NOTE*.
2. Transfer two identical size samples of the caustic into separate 250-mL Erlenmeyer flasks, using Table A-1 as a guide. Weigh the samples to the nearest 0.001 g.

Table A-1
Suggested Sample Size

Caustic Concentration, mass-% NaOH	Suggested Sample Size
0 – 2	Pipet 10 mL
2 - 4	Pipet 5 mL
4 - 8	Weigh 2 ± 0.01 g
8 and above	Weigh 1 ± 0.01 g

3. Add approximately 50-mL of water and 50-mL of 2-propanol to each of the flasks.
 - If the samples taken for analysis are too highly colored to determine the proper endpoint, select correspondingly smaller size samples for analysis.
4. Add 2 to 3 drops of bromothymol blue indicator solution to one of the flasks.
5. Titrate with 0.1-*M* hydrochloric acid until the yellow endpoint color appears in the solution. Record the volume of acid used to this endpoint as the bromothymol blue endpoint.
 - This titration represents the strong base in the sample.
6. Add 2 to 3 drops of bromophenol blue indicator solution to the second Erlenmeyer flask.
7. Titrate with 0.1-*M* hydrochloric acid until the yellow-green color endpoint appears in the solution. Record the total volume of acid used to this endpoint as the bromophenol blue endpoint.
 - This titration represents the total alkalinity of the sample.

CALCULATIONS

The expressions used in this *APPENDIX* are brief and typical of those accepted and used by the petroleum refinery chemist. The expression “% Spent” is an approximate, but useful, measure of the condition of a refinery caustic used to remove weak acids.

In the case where the caustic solution is being used as a prewash, primarily for the removal of naphthenic acids, it is useful to have a measure of the strong base available for weak acid removal. The available strong base for this purpose is given in strong base calculated as mass-% free sodium hydroxide, Eq. A-2.

$$\text{Total Alkalinity, as NaOH, mass - \%} = \frac{4.00 \text{ AM}}{W} \quad (\text{A-1})$$

where:

A = total volume of acid used to reach the bromophenol blue endpoint, mL

M = molarity of acid used, mol/L

W = mass of sample, g (volume in mL times sp. gr.)

4.00 = [(molecular weight of NaOH, 40.0 g/mol)(100%)] / (1000 mL/L)

$$\text{Strong Base, as NaOH, mass - \%} = \frac{4.00 \text{ BM}}{W} \quad (\text{A-2})$$

where:

B = total volume of acid used to reach the bromothymol blue endpoint, mL
M, W and 4.00 = as previously defined, Eq. A-1

$$\% \text{ Spent} = 100 \frac{(a - b)}{a} \quad (\text{A-3})$$

where:

a = total alkalinity, mass-%, as calculated in Eq. A-1
b = strong base, mass-%, as calculated in Eq. A-2

Alternatively, the % Spent can be calculated as follows, providing the same size sample is used in each titration.

$$\% \text{ Spent} = 100 \frac{(A - B)}{A} \quad (\text{A-4})$$

where:

A = as previously defined, Eq. A-1
B = as previously defined, Eq. A-2

NOTE

The difference between total alkalinity by titration and that approximated by specific gravity is an indication of non-titratable neutral salts present in the sample.

PRECISION

An estimated standard deviation is not reported since insufficient data are available to permit this calculation.

TIME FOR ANALYSIS

The elapsed time for one analysis is 1.5 hours. The labor requirement is 1.0 hour.

REFERENCE

ASTM Method D 1298, www.astm.org

“Density, Refractive Index, Freezing Point Depression and Viscosity of Aqueous Solutions,” *CRC Handbook of Chemistry and Physics*, pp. 8 through 74, 77th Ed., **1996-97**, CRC Press, Inc., 2000 Corporate Blvd., N.W., Boca Raton, FL 33431

SUGGESTED SUPPLIERS

Same as listed in the body of the method.