

CAUSTIC SOLUTION ANALYSIS – DOUBLE INDICATOR

UOP Method 210-76T

SCOPE

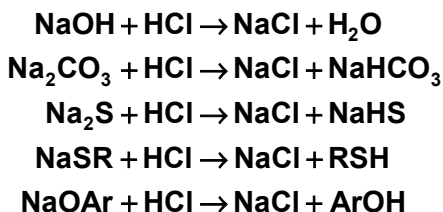
This method is a convenient, though not rigorous, test for the plant control of refinery caustic solutions used to remove hydrogen sulfide, mercaptans and certain other weak acids from petroleum products. The method is also applicable to Merox circulating caustic. The results are significant only when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

While the *Double Indicator Procedure* may be a convenient procedure to use, a potentiometric procedure is more accurate and can distinguish between strong bases; i.e., sodium phenolate and sodium hydroxide. See UOP Method 209.

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 a second sample are then titrated with standard acid to the bromphenol blue endpoint to determine total alkalinity.

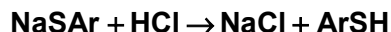
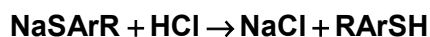
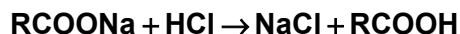
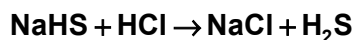
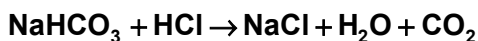
The titration of the strong bases to the bromthymol blue endpoint includes sodium hydroxide, 1/2 the sodium carbonate, 1/2 the sodium sulfide, sodium alkyl mercaptides and sodium phenolates:



where ArOH represents a generic formula for phenols.

The titration of a second sample of the caustic to the bromphenol 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):

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).



Sodium thiosulfate interferes with the bromphenol blue endpoint in that the endpoint slowly fades. However, this is not a serious drawback since this method is intended merely as a control, or 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. The difference between total alkalinity by titration and that approximated by specific gravity is an indication of non titratable neutral salts present.

APPARATUS

Buret, 50 - and 100 - mL

Cylinder, graduated

Flasks, Erlenmeyer, 250 - mL

Flasks, volumetric, 250 - mL

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°.

Pipets, 5 - and 10 - mL

REAGENTS

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

Bromphenol blue indicator solution. Dissolve 0.1 g of bromphenol blue in 7.5 mL of 0.02-*N* sodium hydroxide and dilute with water to 250 - mL.

Bromthymol blue indicator solution. Dissolve 0.1 g of bromthymol blue in 7.5 mL of 0.02-*N* sodium hydroxide and dilute with water to 250 - mL.

Hydrochloric acid, aqueous, 0.100-*N*, standardized

Isopropyl alcohol, 98-99% pure

PROCEDURE

Obtain a sample of the caustic solution and determine the specific gravity at room temperature by means of the appropriate hydrometer. Refer to any appropriate published table to convert the specific gravity of the sample to the approximate total alkalinity as weight - percent sodium hydroxide.

Size the sample for analysis according to the following table:

Caustic Concentration, wt - % NaOH	Sample Size
0 - 2	Pipet 10 ml $\pm$ 0.1 mL
2 - 4	Pipet 5 ml $\pm$ 0.05 mL
4 - 8	Weigh 2 g $\pm$ 0.01 g
8 and above	Weigh 1 g $\pm$ 0.01 g

Pipet or weigh two identical size samples of the caustic into separate 250 - mL Erlenmeyer flasks, using the table as a guide.

Add 50-mL of water and 50-mL of isopropyl alcohol to each of the flasks. Add a few drops of bromthymol blue indicator solution to one of the flasks. Titrate with 0.1 *N* hydrochloric acid until the yellow endpoint color appears in the solution. Record the milliliters of acid used to this endpoint as the bromthymol blue endpoint. This titration represents the *strong* base in the sample.

To the second Erlenmeyer flask add a few drops of bromphenol blue indicator solution and titrate until a yellow - green color endpoint appears in the solution. Record the total milliliters of 0.1 *N* acid used to this endpoint as the bromphenol blue endpoint. This titration represents the *total* alkalinity of the sample.

If the color of the samples taken for analysis are too highly colored to determine the proper endpoint, select correspondingly smaller size samples for analysis.

CALCULATIONS

The expressions used in this method 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 (b) strong base calculated as weight - percent free sodium hydroxide.

$$(a) \text{ Total alkalinity, as NaOH, wt - \% } = \frac{4.0AN}{W}$$

where:

A = total volume of acid to the bromphenol blue endpoint, ml

N = normality of the acid

W = weight of sample (mL x sp. gr.), g

$$(b) \text{ Strong base, as NaOH, wt - \%} = \frac{4.0BN}{W}$$

where:

B = volume of acid to bromthymol blue endpoint, mL

N and **W** are as previously defined

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

where:

a = total alkalinity, wt-%, as calculated in (a) above

b = strong base, wt-%, as calculated in (b) above

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

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

where:

A and B are as previously defined

PRECISION

An estimated standard deviation is not reported since insufficient data are available at present to permit this calculation with at least four degrees of freedom.

TIME FOR ANALYSIS

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