

CAUSTIC SOLUTIONS ANALYSIS —LIBERATION METHOD

UOP Method 211-79

SCOPE

This method is for plant control analysis of used refinery caustic solutions. It is especially useful for solutions containing Merox[®] catalyst used for the extraction or sweetening of mercaptans. Two characteristics of a used caustic solution are determined; namely, total alkalinity and the caustic consumed by the presence of mercaptan. Free sulfur and polysulfide sulfur may interfere with the test. Hydrogen sulfide does not interfere.

OUTLINE OF METHOD

Alkalinity is determined by potentiometric titration. The mercaptide content is determined by acidifying a sample and extracting the mercaptans with isooctane, and then titrating the extract potentiometrically with silver nitrate.

APPARATUS

Burets, 50-ml

Cylinders, mixing, 250-ml, graduated, glass-stoppered

Pipets, 5-, 10-, 25-, 50- and 100-ml

Potentiometric titration equipment, including calomel, glass, and silver-silver sulfide electrodes. See UOP Method 163 for a description of this equipment.

REAGENTS

All reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society where such specifications exist, unless otherwise specified.

Acid, standard 1-N, sulfuric or hydrochloric

Ammonia, aqueous, concentrated

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).

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Hydrochloric acid, concentrated

Isooctane, oxygen-free. Purge ASTM Knock Test grade isooctane for 1 hour with nitrogen and store under nitrogen.

Isopropyl alcohol, oxygen-free. Purge the contents of a freshly-opened bottle with nitrogen for 1 hour and store under nitrogen.

Mercury, metallic

Silver nitrate solution, alcoholic or aqueous, standard 0.01 *N* and 0.1 *N*.

Water, distilled or deionized

PROCEDURE

Determine the specific gravity of the sample if unknown.

A. Total Alkalinity

Pipet a 5- or 10-ml sample into a titration beaker and dilute with about 50 ml of water. Titrate the solution potentiometrically with standard 1*N* acid using a glass and calomel electrode pair. Take the endpoint for total alkalinity as that break in the titration curve nearest to pH 3 to get the total alkalinity. Ignore any breaks in the titration which may occur at higher pH values because these do not represent the total alkalinity.

B. Sodium Hydroxide Spent, as Sodium Mercaptide

Purge the air from a 250-ml mixing cylinder with nitrogen. Pipet in 100 ml of the oxygen-free isooctane while keeping the nitrogen line in the upper portion of the cylinder to prevent air from entering. Pipet into the cylinder the volume of caustic selected from the sample size table below. Add from a buret an amount of concentrated hydrochloric acid calculated from the total alkalinity determined in Section A, above, to just neutralize the caustic, plus 0.2 to 0.5 ml of excess acid. Avoid a large excess of acid.

Sample Size Selection

Expected Mercaptide, Calculated as % S	Sample Size, ml	Normality of Silver Nitrate Solution
0.0000 - 0.0025	50	0.01
0.0025 - 0.0100	25	0.01
0.0100 - 0.0500	10	0.01
0.0500 - 0.2000	5	0.01
0.2000 - 1.00	10	0.1
1.00 - 2.00	5	0.1
2.00 - 5.00	1	0.1

Remove the nitrogen line and immediately stopper the cylinder. Avoid any contact with air as it will cause low results. Gently slosh the contents back and forth a few times to extract the mercaptans. Too vigorous shaking will cause methylmercaptan to vaporize and blow off the stopper. Allow the contents of the cylinder to settle.

Place 100 ml of oxygen-free isopropyl alcohol and 2 to 3 ml of concentrated ammonia in a titration beaker. Then pipet in 50 ml of the isooctane-mercaptan solution. Test another portion of the isooctane with lead acetate paper or doctor solution to determine if hydrogen sulfide is present. Immediately titrate the mercaptan potentiometrically with 0.01 *N* or 0.1 *N* alcoholic or aqueous silver nitrate solution, using a glass and silver-silver sulfide electrode pair (see UOP Method 163 for a description of the silver-silver sulfide electrode). If hydrogen sulfide is present, note the occurrence of the first break and titrate to the second break. Take the net difference between the two breaks as the mercaptan titration.

Elementary sulfur interferes and if present, must be removed by shaking the isooctanemercaptan extract with metallic mercury in the complete absence of air. Otherwise, low values for the mercaptan content will be obtained.

CALCULATIONS

A. Total Alkalinity

Total alkalinity, calculated as

$$\text{wt-\% NaOH} = \frac{V \times N \times 4.00}{A \times G}$$

where:

V = volume of standard acid used, ml

N = normality of standard acid

A = volume of sample titrated, ml

G = specific gravity of sample

B. Spent Caustic as Sodium Mercaptide

Mercaptan, calculated as

$$\text{wt-\% NaOH} = \frac{V_s \times N_s \times 8.00^*}{A_s \times G}$$

where:

V_s = volume of standard silver nitrate used to titrate mercaptan, ml

N_s = normality of silver nitrate

A_s = volume of sample extracted, ml

G = specific gravity of sample

*Change the 8.00 to 6.41 if calculation of wt-% mercaptan sulfur is desired.

NOTES AND PRECAUTIONS

There are sulfur compounds in Merox-containing caustic, at present unidentified but believed to be partially oxidized, that interfere with the direct mercaptan titration. Hence it is necessary to liberate and extract the mercaptan and determine the mercaptan content of the extract.

Traces of oxygen interfere seriously in this test by sweetening the mercaptan. Extreme care must be taken to rigorously exclude air, both during sampling at the plant and while analyzing the sample.

The size of sample and the amount of isooctane used have been developed for caustic samples containing methyl mercaptide, such as those from a butane scrubber. Because of the volatility of methyl mercaptan, the volume ratio of isooctane to sample is critical and must be kept at least as large as shown in the sample size table. If too much methyl mercaptan is liberated from the caustic, some of it will vaporize from the isooctane.

No trouble has been encountered with samples containing higher boiling components, provided that sufficient ammonia is present to neutralize all the acids extracted from the sample. It can be assumed that sufficient ammonia is present if the titration solvent-isooctane mixture smells of ammonia.

PRECISION

More than 90% of the mercaptan sulfur is recovered in this method.

REFERENCE

UOP Method 163