

ACID OILS IN REFINERY CAUSTIC BY LIBERATION

UOP Method 743-73T

SCOPE

This method is for determining the concentration of acid oils in refinery caustic. Part “A”, separation of the acid oils by gravity, is a rapid determination for control purposes. The acid oil concentration range which can be determined is from 1 liquid volume percent (LV-%) upward, with no maximum limit. Part “B”, separation of the acid oils by extraction, is reserved for a more precise gravimetric procedure as well as a volumetric measurement. It is applicable to caustic samples containing as little as 0.1 wt- % acid oil.

OUTLINE OF METHOD

Part A

A known volume of sample is acidified with dilute hydrochloric acid and transferred to a separatory funnel. The acid oils are allowed to separate from the solution by gravity. The acidified caustic solution is drained off and a volume measurement is made of the remaining acid oils.

Part B

The weighed sample of refinery caustic of known volume is acidified with dilute hydrochloric acid and transferred to a separatory funnel. The acid oils are extracted with ether. The ether layer is separated from the acidified caustic solution and the ether is evaporated. The oil residue remaining is weighed. In addition, the volume is measured.

APPARATUS

Balance, torsion or equivalent, capable of weighing 500 g to the nearest 0.1 g.

Beakers, glass, 50-, 100-, 250-, 500- and 1000-ml

Cylinders, graduated, 5-, 25-, 100- and 250-ml

Funnels, separatory, 250- and 500-ml

Gloves, plastic or rubber

Stirring rod, glass

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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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 unless otherwise specified.

Ethyl ether

Hydrochloric acid, concentrated

Hydrochloric acid, dilute. Dilute 1 volume of hydrochloric acid with 1 volume of water.

pH paper

PROCEDURE

Since refinery caustic samples can contain very foul-smelling compounds, such as mercaptans, phenol, cresols and thiophenols, it is strongly recommended that the entire analysis be carried out in a well-ventilated hood. Also, because ether is used in the extraction step of Part B, allow no open flames or operating electrical equipment in the hood.

Part A – Acid Oils by Gravity Separation

Prior to taking a sample, shake the sample container to ensure a uniformly mixed sample. Transfer into a clean, dry 500-ml beaker 100-200 ml of the caustic sample. Measure the volume of sample taken to the nearest 0.5 ml. Place the beaker containing the sample in a 1000-ml beaker containing iced tap water. Slowly add dilute hydrochloric acid to the caustic with constant stirring until the pH of the solution is approximately 3, as determined by occasionally touching a strip of pH paper with solution adhering to the stirring rod.

Remove the beaker from the ice water and allow the solution to come to room temperature. Transfer the solution to a 250- or 500-ml separatory funnel and allow the acid oils to separate from the solution by gravity. For complete separation allow the solution to stand for 30 minutes.

Drain and discard the lower (aqueous) layer. Transfer the upper (acid oil) layer to an appropriately-sized graduated cylinder and measure the volume to the nearest 0.1 ml.

Part B – Acid Oils by Extraction

Prior to taking a sample, shake the container to ensure a uniformly mixed sample. Transfer into a tared, clean, dry 500-ml beaker a 100-200 ml sample of the caustic, measured to the nearest 0.5 ml. Reweigh the beaker to the nearest 0.1 g. Place the beaker in a 1000-ml beaker containing iced tap water. Slowly add dilute hydrochloric acid to the caustic with constant stirring until the pH of the solution is approximately 3, as determined by occasionally touching a strip of pH paper with solution adhering to the stirring rod.

Remove the beaker from the ice water and allow the solution to come to room temperature. Transfer the solution to a 250- or 500-ml separatory funnel. Wash the beaker with 100 ml of ether and add the washing to the separatory funnel.

Stopper the separatory funnel, invert it once or twice and quickly vent the funnel of any pressure. Repeat this venting until no excessive pressure is developed, then shake for 1 minute. Allow the ether-acid oil

phase to separate from the aqueous phase. Drain off the aqueous phase into a second separatory funnel. Include in the aqueous solution a small volume of the ether extract to ensure all the aqueous portion is removed.

To the aqueous layer in the second funnel add 100 ml of ether and follow the same procedure used in the first extraction. After the ether phase has separated, drain the aqueous phase plus a small amount of ether into a 500-ml beaker. Drain the remaining ether into the separatory funnel containing the ether from the first extraction. Continue the ether extraction of the acidified caustic solution until the ether extract is water white. Generally, three 100-ml ether extractions are sufficient to remove all the acid oils.

Drain any aqueous material from the bottom of the combined ether extracts. Drain the ether extract into a clean, dry 500-ml beaker. Set the beaker in a 1000-ml beaker containing warm tap water (not over 100 F) and allow the ether to boil off to a volume of about 50-ml. Transfer the concentrated ether extract to a tared 100 - ml beaker. Allow the remaining ether to boil off in warm tap water until there is no longer an odor of ether. Reweigh the beaker to the nearest 0.1 g, then transfer the acid oils to an appropriately-sized graduated cylinder and measure the volume to the nearest 0.1 ml.

CALCULATIONS

Part A – Acid Oils by Gravity Separation

$$\text{Acid oils, LV-\%} = \frac{100 A}{B}$$

where:

A = volume of acid oils separated from the sample, ml

B = volume of sample taken for analysis, ml

Part B – Acid Oils by Extraction

$$\text{Acid oils, LV-\%} = \frac{100 C}{D}$$

where:

C = volume of acid oils recovered, ml

D = volume of sample taken for analysis, ml

$$\text{Acid oils, wt-\%} = \frac{100 E}{F}$$

where:

E = weight of acid oils recovered, g

F = weight of sample taken for analysis, g

NOTES AND PRECAUTIONS

Wear protective gloves while handling caustic samples as well as the extracted acid oils.

Work in a hood at all times if the analysis is conducted indoors.

Carry out disposal of caustic samples in an environmentally safe manner.

PRECISION

An estimated standard deviation is not reported since insufficient data are available at present to permit this calculation with at least 4 degrees of freedom.

TIME FOR ANALYSIS

Acid Oils by Gravity Separation

The labor requirement is 0.5 for 1 analysis and elapsed time is 1 hour.

Acid Oils by Extraction

The labor requirement is 1 man-hour for 1 analysis and elapsed time is 3 hours.