

Determination of Sulfides

Objective

Determine the amounts of sodium sulfide, sodium hydrosulfide, and sodium hydroxide in caustic sulfide solutions.

Introduction

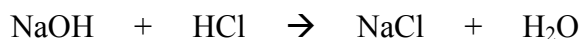
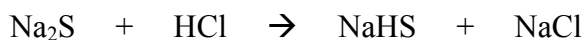
Sulfide concentrations are extremely important in petroleum refining. Crude oil has varying amounts of sulfur depending on the source of the crude. Crude can be categorized into two categories: sweet crude and sour crude. Originally smell and taste were used to determine the difference between sweet and sour crudes. Sour crudes (which are high in sulfur) have an unacceptable smell when burned. Sweet crudes do not. Kerosene (a product of the distillation of crude oil) was tasted to determine if it was suitable for use at market. If the taster deemed it sweet, it was sent to market, if it was sour, it was rejected. The taste test is no longer used to determine the sulfur content. Today, sweet crudes typically have 0.5% sulfur or less, while sour crudes have 2.5% or more. In between 0.5% and 2.5%, the distinctions of intermediate sweet and intermediate sour are used.

The sulfur that is present in crude oil is not usually in the form of elemental sulfur. Instead, the sulfur is found bonded to other atoms to create sulfur compounds, including hydrogen sulfide, sodium sulfide and mercaptans. A mercaptan is a petroleum hydrocarbon that contains sulfur.

To determine the presence of hydrogen sulfide and/or mercaptans, the doctor test may be performed. This test is run by shaking the sample with sodium plumbite solution, adding a pinch of flowers of sulfur and shaking again. An immediate black precipitate before the sulfur addition indicates hydrogen sulfide. In the absence of hydrogen sulfide, but in the presence of mercaptans, the color change is frequently gradual going through orange, red, and brown to black.

After testing positive for sulfides, the solution is often tested to determine the amount of sulfides present. A titrimetric procedure is used to perform this test.

In this method, sulfide is first titrated to hydrosulfide with thymolphthalein as indicator, then formaldehyde is added and all of the hydrosulfide is titrated.



When formaldehyde is added to the hydrosulfide solution, an equivalent amount of sodium hydroxide is formed, which is then titrated with acid. With pure sulfide, (A) is equal to (B). If (A)

exceeds (B), the difference represents free alkali, while if (B) is greater than (A), the difference is a measure of the original hydrosulfide.

When (A) is greater than (B):

$$\text{Na}_2\text{S, lb./bbl.} = \frac{27.32 \times N \times (B)}{\text{ml of sample}}$$

$$\text{NaOH, lb./bbl.} = \frac{14 \times N \times (A - B)}{\text{ml of sample}}$$

When (B) is greater than (A):

$$\text{Na}_2\text{S, lb./bbl.} = \frac{27.32 \times N \times (A)}{\text{ml of sample}}$$

$$\text{NaOH, lb./bbl.} = \frac{14 \times N \times (B - A)}{\text{ml of sample}}$$

Where:

(A) = ml of acid to the first endpoint

(B) = ml of acid from first end point to second end point

(N) = normality of acid

Materials

25 ml graduated cylinder

1 ml pipette

250 ml Erlenmeyer flask

50 ml burette

Reagents

Unknown sample to be titrated

Distilled water

Thymolphthalein solution (1% in alcohol)

Phenolphthalein solution (1% in alcohol)

0.1786 N Hydrochloric Acid

Neutralized formaldehyde solution:

Add 10 drops of phenolphthalein solution to approximately 500 ml of formaldehyde solution in a glass-stoppered bottle. Add 20% sodium hydroxide solution drop by drop, with mixing between each addition, until the formaldehyde has a faint pink color when viewed against a white background. If the solution becomes colorless on standing, again add a drop or two of sodium hydroxide solution to bring it back to a faint pink color before using. Filter or decant before using when a white deposit is present in the bottle.

Procedure

1. Measure approximately 25 ml of distilled water into a 250 ml Erlenmeyer flask.
2. Pipette 1 ml of the sample into the Erlenmeyer flask.
3. Add 5 drops of thymolphthalein solution.
4. Fill a buret with 0.1786 N hydrochloric acid.
5. Record the initial volume of hydrochloric acid in the buret on the data sheet.
6. Titrate the sample to a pale blue color (with the 0.1786 N hydrochloric acid).
7. Record final volume of hydrochloric acid in the buret on the data sheet.
8. Calculate the amount of acid used in ml (A) and record on the data sheet.
9. Add 1 drop of phenolphthalein solution to the Erlenmeyer flask.
10. Add 10 ml of neutralized formaldehyde solution to the flask. The solution usually will again become deep blue, or if little sulfide is present, a pink or purple color will be noted.

11. Continue the titration with acid to a faint pink color, allow the solution to stand about 3 minutes, then complete the titration to a colorless end point.
12. Record as the volume of acid used between the first and second end points (B) on the data sheet.
13. Repeat the procedure.
14. Perform calculations and record results on the data sheet.
15. Attach all papers used to make calculations.
16. Clean entire work area and dispose of wastes as instructed.

DATA

	Trial 1	Trial 2
Initial reading on buret (before titration)	_____	_____
Reading on buret at first end point	_____	_____
Reading on buret at second end point	_____	_____
Amount of acid used for first end point (calc) (A)	_____	_____
Amount of acid used for second end point (calc) (B)	_____	_____
Which is greater, (A) or (B)?	_____	_____
Amount of Na ₂ S	_____	_____
Average amount of Na ₂ S	_____	

If (A) is greater than (B):

Amount of NaOH

Average amount of NaOH

If (B) is greater than (A):

Amount of NaHS

Average amount of NaHS
