

APPARENT HYDROGEN SULFIDE IN AMINE SOLUTIONS

UOP Method 827-81

SCOPE

A Control and a Precision method are used for the determination of apparent hydrogen sulfide in amine solutions. Hydrogen sulfide is determined by oxidation with standard iodine solution in an acid medium. Thiosulfate, if present, is also titrated and is included as apparent H₂S in the calculation. Thiosulfate may be determined by using UOP Method 818, and the value thus obtained subtracted from the apparent H₂S concentration. The lower limit of detection is approximately 25 grains/gallon.

OUTLINE OF METHOD

Control Method

For plant control work with lean amine solutions containing low levels of hydrogen sulfide, a direct titration method may be used. A portion of the amine sample is pipeted into water, acidified with HCl, and immediately titrated with a standard iodine solution using starch solution as the indicator.

Precision Method

For solutions containing more than 100 grains of H₂S per gallon, or where better precision is required, a portion of the amine sample is pipeted into an acidified water solution containing an excess of standard iodine solution. The excess iodine is back titrated with standard sodium thiosulfate solution using starch solution as the indicator.

APPARATUS

Balance, torsion or top loading type, 500 g capacity, capable of weighing to 0.01 g

Beakers, 100- and 250-mL

Buret, 50-mL (2 required) with Teflon stopcock, 0.1-mL subdivisions

Cylinder, graduated, 50-mL, glass, 1.0-mL subdivisions

Flask, Erlenmeyer, 250-mL

Flask, volumetric, one-liter (2 required)

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Flask, volumetric, 100-mL

Hot plate, adjustable heat, Sargent-Welch Scientific Co., Cat. No. S-41000A, or equivalent

Pipet manipulator, Sargent-Welch Scientific Co., Cat. No. S-69793, or equivalent

Pipets, serological, calibrated for blow-out, 1-, 5- and 10-mL capacity, Sargent-Welch Scientific Co., Cat. Nos. S-69625-C, G and H, or equivalent

Stirrer, magnetic, with Teflon covered stirring bar, Sargent-Welch Scientific Co., Cat. No. S-76490, or equivalent

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.

Hydrochloric acid, concentrated

Iodine solution, 0.05 *M*. To prepare, dissolve 25 g of potassium iodide in 200 mL of water. Warm slightly to dissolve. Cool and add 12.69 g of iodine crystals. Stir the solution to dissolve the reagents and transfer quantitatively to a one-liter volumetric flask. Dilute to volume with water. Store in an amber bottle. Standardize against the 0.1 *M* sodium thiosulfate. If samples are analyzed infrequently, the iodine solution must be standardized prior to use.

Methyl orange indicator solution, 0.1 wt-% concentration. Dissolve 0.1 g of methyl orange in 100 mL of water.

Salicylic acid

Sodium thiosulfate solution, 0.1 *M*. To prepare, dissolve 24.82 g of sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) in 200 mL of warm water. Quantitatively transfer to a one-liter volumetric flask, cool, and dilute to volume with water. Standardize in any acceptable fashion such as by the iodine or arsenious oxide technique.

Starch, arrowroot, Leco Corp., Cat. No. 501-061, or equivalent

Starch solution. Stir with a glass rod while slowly adding 0.25 g of starch to 10 mL of water in a 100-mL beaker. Quantitatively transfer the resulting solution to a 100-mL volumetric flask containing 60-70 mL of hot, 95-100 C, water. Swirl the flask to mix. Add 0.12 g of salicylic acid, predissolved in 5 mL of warm water, to the flask as a preservative. Cool the flask and contents to room temperature and dilute to volume with water. A fresh solution must be prepared if a mold appears or when a definite blue color is not obtained with iodine solution.

PROCEDURE

Arrange the apparatus in an efficient hood to avoid any hazard from the evolution of gaseous H_2S .

Determine the amount of sample to be taken for analysis from the following table:

Apparent H₂S concentration expected in the sample, grains/gallon	Sample size, mL
> 100	1.0
< 100	5.0-10.0

Control Method

Pipet the appropriate size sample into a 250-mL Erlenmeyer flask containing a magnetic stirring bar and 100 mL of water. With viscous samples, rinse the pipet with water and add the rinsings into the flask. Pipet a volume of concentrated HCl, equal to the sample size taken, into the flask. Add approximately 2 mL of starch indicator solution. Turn on the magnetic stirrer and titrate immediately with standard 0.05 *M* iodine solution until a deep-blue color persists.

Precision Method

To a 250-mL Erlenmeyer flask containing a magnetic stirring bar, add 50 mL of water and 25 mL of standard iodine solution (measured to the nearest 0.1 mL from the iodine buret). Add a volume of concentrated HCl to the flask equal to the volume of amine solution to be taken (see Notes 1, 2 and 3). Turn on the magnetic stirrer and pipet the amine sample into the flask. With viscous samples, rinse the pipet with water and add the rinsing into the flask.

If the acidified sample is not darkly colored before the addition of the iodine solution, titrate with the standard sodium thiosulfate solution until the sample-solution is almost colorless, then add 2 mL of starch indicator solution and continue the titration until the sample-solution is colorless. If the acidified sample is colored, add starch immediately and titrate with the standard sodium thiosulfate solution until the blue color disappears. Test the sample-solution with methyl orange indicator to verify that the solution is sufficiently acid. If the solution is not acid (red colored), repeat the analysis but this time add 25% more concentrated hydrochloric acid (see Note 3).

CALCULATIONS

Calculate the concentration of apparent hydrogen sulfide in the sample solution as follows:

Control Method

$$\text{Apparent H}_2\text{S, grains/gallon} = \frac{1991 AM_1}{V}$$

where:

A = standard iodine solution added, mL

M₁ = molarity of the iodine solution

V = sample volume, mL

Precision Method

$$\text{Apparent H}_2\text{S, grains/gallon} = \frac{1991 (AM_1 - 0.5BM_2)}{V}$$

where:

B = standard sodium thiosulfate solution, mL
M₂ = molarity of the sodium thiosulfate solution
A, **M₁** and **V** are as previously defined

The apparent hydrogen sulfide concentration in grains/gallon may be converted to volumes of hydrogen sulfide, as a dry gas at 15.6 C (60 F) and 101.3 kPa (760 mm), to volume of solution by dividing by 84.

The apparent hydrogen sulfide concentration may be converted to wt-ppm as follows:

$$\text{Apparent H}_2\text{S, wt - ppm} = \frac{17C}{S}$$

where:

C = apparent H₂S content, grains/gallon
S = specific gravity of sample, 60/60 F (15.6/15.6 C)

NOTES

1. The volume of standard iodine solution is varied with the hydrogen sulfide content of the amine solution sample. Sufficient iodine solution should be taken so that about 10 mL of standard sodium thiosulfate solution are required for back titration.
2. When the amine sample solution is concentrated and viscous, it is preferable to pipet the sample into an Erlenmeyer flask, containing 50 mL of water. Rinse the pipet with water into the flask. The diluted sample is then mixed with the acidified iodine solution. This procedure prevents the local neutralization of the iodine by strong amine solution.
3. Free amine reacts quite rapidly with iodine solution and it is, therefore, necessary that the amine solution come in contact with the iodine only in the presence of excess acid.

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. It is estimated that duplicate analyses should agree within 25 grains/gallon for both the control and precision methods.

TIME FOR ANALYSIS

The elapsed time for one analysis is 1.0 hour. The labor requirement is 0.5 hour.

REFERENCES

Method SM-6, The Girdler Corp., Louisville, KY

SUGGESTED SUPPLIERS

Leco Corp., 300 Lakeview Ave., St. Joseph, MI 49085
 Sargent-Welch Scientific Co., 7300 N. Linder Ave., Skokie, IL 60076