Modified May 21, 1979
Laboratory Division
Texas Air Control Board

DETERMINATION OF HYDROGEN SULFIDE IN STACK GAS

A. GENERAL

Hydrogen sulfide (H_2S) is absorbed in a zinc acetate [$Zn(C_2H_3O_2)_2$] absorber. The sulfide in the absorber is measured by titration of excess iodine with standard thiosulfate using a starch indicator.

B. APPLICABILITY

The lower limit of detectability has been found to be 0.1 mg/ml of H_2S in the absorbing reagent. If levels lower than this are desired, then the molybdenum blue method should be used. Zinc acetate is recommended as the absorber for high levels of sulfide such as in stack sampling, since it absorbs H_2S more efficiently than does alkaline cadmium sulfate at high H_2S levels. Loss of sulfide by oxidation occurs with zinc acetate but is significant only at low sulfide levels. Therefore, alkaline cadmium sulfate is used for ambient and property line sampling. (See Determination of Hydrogen Sulfide - Molybdenum Blue Method.)

C. APPARATUS

Suitable sampling apparatus
Adequate and sufficient storage bottles
4-1000 ml volumetric flasks
1-1000 ml beaker
9-250 ml Erlenmeyer flasks or 250 ml beakers
1-50 ml pipet
2-25 ml pipets
1-50 ml buret

D. REAGENTS

All reagents should be ACS reagent grade.

(1) Iodine, 0.1 N
Dissolve 12.7 grams of resublimed iodine in 25 ml of a solution containing 15 grams of potassium iodide. Stir until all the iodine is dissolved. Dilute to one liter with distilled or deionized water. Store in a dark bottle.

(2) Sodium Thiosulfate, 0.1 N

Weigh 16.0 grams of anhydrous sodium thiosulfate ($Na_2S_2O_3$) (25g $Na_2S_2O_3 \cdot 5 H_2O$) and 1g Na_2CO_3 and dilute to one liter. Use this solution to standardize the iodine solution. Sodium thiosulfate is fairly unstable and should be standardized before each use.

(3) Potassium Dichromate 0.100 N

Using an analytical balance, accurately weigh out 4.9036 grams of oven-dried $K_2Cr_2O_7$. Dissolve this in distilled or deionized water in a 1000 ml volumetric flask and dilute to the mark with distilled or deionized water. This solution is 0.100 N and is stable.

(4) Starch Indicator Solution

Dissolve 2 grams of reagent grade soluble starch in 500 ml of boiling distilled water. Then filter while the solution is still warm and add a crystal or two of mercuric chloride to inhibit mold growth.

(5) Absorbing Reagent - Zinc Acetate, 2%*

Dissolve 20 grams zinc acetate [$Zn(C_2H_3O_2)_2$] in approximately 100 ml of deionized or distilled water and dilute to 1 liter. A precipitate will form. Before withdrawing any of this solution, agitate the solution well in order to get the precipitate sus-pended so that a representative aliquot will be obtained.

*Zinc sulfide (formed when H_2S is absorbed) adheres to glass surfaces. All glassware which has been in contact with this should be rinsed with a little dilute acid before any other use.

(6) Sodium Sulfide Stock

Dissolve 0.750 grams sodium nonahydrate ($Na_2S \cdot 9 H_2O$) in 200 ml of zinc acetate absorber. Stir until solution is complete. The concentration of Se ion in this solution is approximately 500 ug Se/ml.

E. COLLECTION OF SAMPLE

Samples should be collected according to accepted stack sampling proce-dures. The sampling lines should be made of FEP^R Teflon or glass. Rubber or metal lines should be avoided.

F. TEST PROCEDURE

(1) Standardization of 0.1 N Sodium Thiosulfate

Into each of three Erlenmeyer flasks or beakers pipet 50 ml of 0.100 N $K_2Cr_2O_7$ using a 50 ml volumetric pipet. Add 8 ml of con-centrated HCl to each flask. From this point, handle each flask in-dividually through the titration. To the first flask add 2 g KI, swirl to hasten dissolution. Titrate the liberated iodine at once with thiosulfate until the color begins to lighten. Add 2 ml starch solution and continue the titration. There is a blue to emerald green

color change at the end point. Titrate the second and third samples of thiosulfate the same way. Determine the blank by use of the same amount of KI and HCl in the same volume of water. Correct the volume of thiosulfate for any blank and calculate the normality of the thiosulfate solution.

(2) Standardization of 0.1 N Iodinee

Into each of three Erlenmeyer flasks or three beakers, pipet accurately 20 ml of the iodine solution. Add about 30 ml of distilled water and 1 ml acetic acid. Titrate with 0.1 N sodium thiosulfate solution until the yellow color of the solution is almost gone. Then add 2 ml starch solution and continue the titration until the blue color just disappears. Titrate the second and third samples of the iodine solution in the same way. Calculate the normality of the iodine.e

(3) Standardization of the Sulfide Stock Solutione

Using a volumetric pipet, place 25 ml of theestandardized 0.1 N iodine solution in a beaker or Erlenmeyer flask. Using another volumetric pipet, place 25 ml of the stock sulfide solution in the same container. (Keep solutions in the dark until ready to titrate). Titrate the excess iodine with the standardized 0.1 N thiosulfate solution to the yellow color of dilute iodine. Then add 2 ml of the starch solution and continue the titration until the blue color just

(4) Sample Analysis

Using a graduated cylinder, measure the volume of each sample. Usinge a volumetric pipet, place 25 ml of the standardized 0.1 N iodine solution in a beaker or Erlenmeyer flask. Using another volumetric pipet, place a 25 ml aliquot of the sample in the same container.e (Keep solutions in the dark until ready to titrate). Titrate the excess iodine with the standardized 0.1 N thiosulfate solution to the yellow color of dilute iodine. Then add 2 ml of the starch solution and continue the titration until the blue color just dis-appears.e

NOTE: For low concentrations the Molybdenum Blue Method shoulde be used.

G.e QUALITY CONTROLee

All titrations should be run in triplicate. The sodium thiosulfate, iodine, and stock sulfide should be standardized before each use. Theee relative deviation in the volume of titrant used should be less thanee 5 parts per thousand (5 °/oo). The relative deviation is calculatedee as follows:ee

$$R.D. = \frac{\bar{d}}{\bar{v}} \qquad \bar{d} = \frac{\Sigma |v_i - \bar{v}|}{N}$$

where $\bar{d}$ = average deviation

$\bar{v}$ = arithmetic average of all individual volumes

v_i = individual measuremente

N = number of measurementse

For example:

Three titration volumes, v_i, were found to be 49.80 ml, 49.91 ml, 49.89 ml for the standardization of $Na_2S_2O_3$.

$49.80 + 49.91 + 49.89 = 149.60$ $\qquad \bar{v} = 49.87$

$|v_1 - \bar{v}| = |49.80 - 49.87|$ $\qquad \Sigma|v_i - \bar{v}| = 0.13$

$|v_2 - \bar{v}| = |49.91 - 49.87|$

$|v_3 - \bar{v}| = |49.89 - 49.87|$ $\qquad \bar{d} = \frac{0.13}{3} = 0.04$

$$\text{R.D.} = \frac{0.04}{49.87} = 0.8\ ^{o}/_{oo}$$

therefore the three titrations are acceptable.

Another example:

19.40, 19.39, 19.40 $\qquad \bar{v} = 19.40 \qquad \bar{d} = 0.003$

$$\text{R.D.} = \frac{0.003}{19.40} = 0.2\ ^{o}/_{oo}$$

therefore the titration is acceptable.

Spiked samples should be run to control the accuracy of the analysis. Spiked samples are prepared by adding a known quantity of a standard to an aliquot of sample. Percent recovery can be calculated from the concentrations of the spiked sample, the sample, and the standard.

A suitable spike would be prepared as follows: Using a volumetric pipet, place 25 ml of the standardized 0.1 N iodine solution in a beaker or Erlenmeyer flask. Using volumetric pipets, place 10 ml of stock sulfide solution and 15 ml of sample in the same container (Keep solutions in the dark until ready to titrate). Titrate the excess iodine with the standardized 0.1 N thiosulfate solution to the yellow color of dilute iodine. Then add 2 ml of the starch solution and continue the titration until the blue color just disappears.

$$\text{Percent recovery} = \frac{\text{conc (spike + sample)} - \text{conc (sample)}}{\text{conc (spike)}} \times 100$$

For example:

A sample took 10.00, 10.05, 9.95 ml thiosulfate to titrate. The spike of the same sample took 12.92 ml, 12.87 ml, 12.85 ml thiosulfate.

The normality of the I_2 solution was 0.09889 N. The thiosulfate was 0.003 N.

The spike was prepared as above. The concentration of the stock sulfide was 500.0 µg $S^{=}$/ml

$$\text{conc (spike + sample)} = \frac{(0.09888 \times 25\ \text{ml}) - (0.1003 \times 12.88\ \text{ml})}{(58.82)\ (25\ \text{ml})} =$$

$$\frac{2.472 - 1.292}{(58.82)\ (25)} = 0.0008024\ \text{g/ml} \qquad 802.4\ \mu\text{g } H_2S\text{/ml}$$

$$\text{conc (sample)} = \frac{(0.09888 \times 25\ \text{ml}) - (0.1003 \times 10.00\ \text{ml})}{(58.82)\ (25\ \text{ml})} = \frac{1.469}{(58.82)(25)} =$$

999.0 µg H_2S/ml

$$\text{conc spike} = \frac{500\ \mu\text{g } S^{=}\text{/ml} \times 10\ \text{ml} \times 34\ \text{g } H_2S\text{/mole}}{25\ \text{ml} \qquad 32\ \text{g } S^{=}\text{/mole}} = 212.5\ \mu\text{g } H_2S\text{/ml}$$

$$\%\ R = \frac{(802.4\ \mu\text{g/ml}) - 999.0(15/25)}{212.5\ \mu\text{g/ml}} = \frac{802.4 - 599.4}{212.5\ \mu\text{g/ml}}$$

$$\%\ R = \frac{203\ \mu\text{g/ml}}{212.5\ \mu\text{g/ml}} = 1.015 \times 100 - 96\%$$

A spiked sample should be run with each set of samples. The percent recovery should be between 90%-110%. If not, all steps of the analysis should be examined carefully and the analysis repeated.

H. CALCULATIONS

(1) Standardization of 0.1 N Sodium Thiosulfate

$$\text{Normality of } Na_2S_2O_3 = \frac{(\text{Normality of } K_2Cr_2O_7 \text{ solution})(\text{Volume } K_2Cr_2O_7)}{\text{Volume } Na_2S_2O_3} =$$

$$\frac{(0.100\ \text{N})(50\ \text{ml})}{\text{volume } Na_2S_2O_3 \text{ in ml}}$$

(2) Standardization of 0.1 N Iodine

$$\text{Normality of } I_2 = \frac{(\text{Normality } Na_2S_2O_3)(\text{Volume } Na_2S_2O_3)}{\text{volume } I_2} =$$

$$\frac{(\text{Normality } Na_2S_2O_3)(\text{Volume } Na_2S_2O_3 \text{ in ml})}{20\ \text{ml}}$$

(3) Standardization of Sulfide Stock Solution

$$g\ H_2S/ml\ \text{of stock} = \frac{(N\ I_2 \times \text{volume } I_2) - (N\ Na_2S_2O_3 \times \text{volume } Na_2S_2O_3)}{58.82 \times \text{volume stock } S^= \text{ aliquot}}$$

where

a) (N of I_2 x volume I_2) - (N of $Na_2S_2O_3$ x volume $Na_2S_2O_3$ used) = Meq I_2 used by stock $S^=$ solution

b) Meq I_2 used by stock $S^=$ solution x $\frac{16\ g/eq}{1000\ meq/eq}$ = g $S^=$ in the aliquot

c) $\frac{\text{grams } S^= \text{ in the aliquot}}{\text{volume stock } S^= \text{ used in ml}} \times \frac{34\ g\ H_2S/mole}{32\ g\ S^=/mole}$ = grams H_2S/ml of stock $S^=$ solution

All volumes are in milliliters

(4) Sample Concentration

$$g\ H_2S/ml = \frac{(N\ I_2 \times ml\ I_2) - (N\ Na_2S_2O_3 \times ml\ Na_2S_2O_3)}{(58.82) \times (\text{sample aliquot volume in ml})}$$

where

a) (N I_2 x ml I_2) - (N $Na_2S_2O_3$ x ml $Na_2S_2O_3$) = Meq I_2 used by sample aliquot

b) Meq I_2 used by sample aliquot x (16 g / eq / 1000 meq / eq) = g $S^=$ in the aliquot

c) $\frac{\text{grams } S^= \text{ in the aliquot}}{\text{sample aliquot volume in ml}} \times \frac{34\ g\ H_2S/mole}{32\ g\ S^=/mole}$

g H_2S/ml in sample aliquot

$$g\ H_2S/M^3 = \frac{g\ H_2S/ml \times \text{volume of absorber in ml}}{M^3 \text{ of air sampled}}$$