

METHOD 9034

TITRIMETRIC PROCEDURE FOR ACID-SOLUBLE AND ACID INSOLUBLE SULFIDES

1.0 SCOPE AND APPLICATION

1.1 This procedure may be used as a determinative step for acid-soluble and acid-insoluble sulfides following distillation of the sample by SW-846 Method 9030.

1.2 Method 9034 is suitable for measuring sulfide concentrations in samples which contain 0.2 mg/kg to 50 mg/kg of sulfide.

2.0 SUMMARY OF METHOD

Sulfide is extracted from the sample by a preliminary distillation procedure (See Method 9030) and precipitated in an zinc acetate scrubber as zinc sulfide. The sulfide is oxidized to sulfur by adding a known excess amount of iodine. The excess iodine is determined by titration with a standard solution of phenyl arsine oxide (PAO) or sodium thiosulfate until the blue iodine starch complex disappears. As the use of standard sulfide solutions is not possible because of oxidative degradation, quantitation is based on the PAO or sodium thiosulfate.

3.0 INTERFERENCES

3.1 The iodometric method suffers interference from reducing substances that react with iodine, including thiosulfate, sulfite, and various organic compounds.

3.2 Refer to Method 9030 for a discussion of other sulfide interferences.

4.0 APPARATUS AND MATERIALS

4.1 500 mL flasks.

4.2 Hot plate stirrer.

4.3 25 mL buret.

4.4 Volumetric pipets.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Starch solution - Use either an aqueous solution or soluble starch powder mixtures. Prepare an aqueous solution as follows. Dissolve 2 g soluble starch and 2 g salicylic acid, $C_7H_6O_3$, as a preservative, in 100 mL hot reagent water.

5.4 Iodine solution (approximately 0.025N)

5.5 Dissolve 25 g potassium iodide, KI, in 700 mL of reagent water in a 1-liter volumetric flask. Add 3.2 g iodine, I_2 . Allow to dissolve. Add the type and amount of acid specified in Section 7.3.2. Dilute to 1 liter and standardize as follows.

5.6 Dissolve approximately 2 g KI in 150 mL of reagent water. Add exactly 20 mL of the iodine solution (Section 5.4) to be titrated and dilute to 300 mL with reagent water.

5.6.1 Titrate with 0.025N standardized phenylarsine oxide or 0.025N sodium thiosulfate until the amber color fades to yellow. Add starch indicator solution. Continue titration drop by drop until the blue color disappears.

5.6.2 Run in replicate.

5.6.3 Calculate the normality as follows.

$$\text{Normality (I}_2\text{)} = \frac{\text{mL of titrant} \times \text{normality of titrant}}{\text{sample size in mL}}$$

5.7 Sodium sulfide nonahydrate, $Na_2S \cdot 9H_2O$. For the preparation of standard solutions to be used for calibration curves. Standards must be prepared at $pH > 9$ and < 11 . Protect standard from exposure to oxygen by preparing it without headspace. These standards are unstable and should be prepared daily.

5.8 Titrant.

5.8.1 Standard phenylarsine oxide solution (PAO) (0.025N), C_6H_5AsO . This solution is commercially available.

CAUTION: PAO is toxic.

5.8.2 Standard sodium thiosulfate solution (0.025N), $Na_2S_2O_3 \cdot 5H_2O$. Dissolve 6.205 ± 0.005 g $Na_2S_2O_3 \cdot 5H_2O$ in 500 mL reagent water. Add 9 mL 1N NaOH and dilute to 1 liter.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Refer to Method 9030 for a discussion of sample collection, preservation, and handling.

6.2 Distillates that are not analyzed immediately should be stored in a sealed flask at 4 °C.

7.0 PROCEDURE

7.1 The following iodometric titration procedure is used to quantify the sulfide concentration in the distillate generated by Method 9030.

7.3.1 Pipet a known amount of standardized 0.025N iodine solution (see Section 5.4) in a 500-mL flask, adding an amount in excess of that needed to oxidize the sulfide. Add enough reagent water to bring the volume to 100 mL. The volume of standardized iodine solution should be about 65 mL for samples with 50 mg of sulfide.

7.3.2 If the distillation for acid-soluble sulfide is being used, add 2 mL of 6N HCl. If the distillation for acid-insoluble sulfides is performed, 10 mL of 6N HCl should be added to the iodine.

7.3.3 Pipet the gas scrubbing solutions obtained in Method 9030 to the flask, keeping the end of the pipet below the surface of the iodine solution. If at any point in transferring the zinc acetate solution or rinsing the bottles, the amber color of the iodine disappears or fades to yellow, more 0.025N iodine must be added. This additional amount must be added to the amount from Section 7.3.1 for calculations. Record the total volume of standardized 0.025N iodine solution used.

7.3.4 Prepare a rinse solution of a known amount of standardized 0.025N iodine solution, 1 mL of 6N HCl, and reagent water to rinse the remaining white precipitate (zinc sulfide) from the gas scrubbing bottles into the flask. There should be no visible traces of precipitate after rinsing.

7.3.5 Rinse any remaining traces of iodine from the gas scrubbing bottles with reagent water, and transfer the rinsate to the flask.

7.3.6 Titrate the solution in the flask with standard 0.025N phenylarsine oxide or 0.025N sodium thiosulfate solution until the amber color fades to yellow. Add enough starch indicator for the solution to turn dark blue and titrate until the blue disappears. Record the volume of titrant used.

7.3.7 Calculate the concentration of sulfide using the following equation:

$$\frac{(\text{mL } I_2 \times N I_2) - (\text{mL titrant} \times N \text{ titrant}) \times \left(\frac{32.06 \text{ g}}{2 \text{ eq.}} \right)}{\text{sample weight (kg) or sample volume (L)}} = \text{sulfide (mg/kg or mg/L)}$$

8.0 QUALITY CONTROL

8.1 All quality control data must be maintained and available for reference or inspection for a period of three years. This method is restricted to use by or under supervision of experienced analysts. Refer to Method 9030 for additional quality control guidelines.

8.2 A reagent blank should be analyzed once in twenty analyses or per analytical batch, whichever is more frequent.

8.3 Check standards are prepared from water and a known amount of sodium sulfide. A check standard should be run with each analytical batch of samples, or once in twenty samples. Acceptable recovery will depend on the level and matrix.

8.4 A matrix spiked sample should be analyzed for each analytical batch or twenty samples, whichever is more frequent, to determine matrix effects. If recovery is low, acid-insoluble sulfides are indicated. A matrix spiked sample is a sample brought through the whole sample preparation and analytical process.

9.0 METHOD PERFORMANCE

9.1 Refer to Method 9030 for data on the precision and accuracy of this method.

10.0 REFERENCES

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