WI 150802.08

T 602

DRAFT NO. 5 SARG

DATE May 18, 2021

WORKING GROUP CHAIRMAN N/A

SUBJECT CATEGORY Chemical Properties

RELATED METHODS See "Additional Information"

CAUTION:
This Test Method may include safety precautions which are believed to be appropriate at the time of publication of the method. The intent of these is to alert the user of the method to safety issues related to such use. The user is responsible for determining that the safety precautions are complete and are appropriate to their use of the method, and for ensuring that suitable safety practices have not changed since publication of the method. This method may require the use, disposal, or both, of chemicals which may present serious health hazards to humans. Procedures for the handling of such substances are set forth on Material Safety Data Sheets which must be developed by all manufacturers and importers of potentially hazardous chemicals and maintained by all distributors of potentially hazardous chemicals. Prior to the use of this method, the user must determine whether any of the chemicals to be used or disposed of are potentially hazardous and, if so, must follow strictly the procedures specified by both the manufacturer, as well as local, state, and federal authorities for safe use and disposal of these chemicals.

Analysis of sulfuric acid

(Proposed REAFFIRMATION of T 602 cm-06 as a Classical Method)

(No changes from previous drafts, Standard reaffirmed)

1. Scope

1.1 This method describes analytical procedures for the testing of sulfuric acid used in pulp and paper manufacture to determine total acidity, Baumé gravity, nonvolatile matter, iron, sulfur dioxide, and arsenic.

1.2 Elaboration on the significance of these procedures, except as shown below, is not within the scope of this method.

2. Significance

2.1 The use of sulfuric acid includes its application in the manufacture of chlorine dioxide for pulp bleaching, the manufacture of tall oil, and for pH control in various processes.

2.2 The value of these analytical procedures is related to production efficiency, quality of product, safety of production personnel, and health of users.

3. Safety precautions

3.1 Sulfuric acid is a strong corrosive acid and is dangerous if improperly handled. Avoid any skin contact. *Analyst must wear goggles with side shields at all times and wear long sleeve rubber gloves and splash apron when sampling or pouring.* If acid is spilled on the skin, wash immediately with large amounts of water. If splashed into the eyes, wash the eyes with water for at least 15 min. Get immediate medical attention.

3.2 *Clean all spills immediately*. Refer to Material Safety Data Sheet for proper cleanup methods, and disposal of spilled material.

4. Sampling

4.1 Sampling of sulfuric acid is not within the scope of this method. For general guidance in sampling, consult ASTM E 300 “Recommended Practice for Sampling Industrial Chemicals.”

4.2 The sample to be analyzed is considered to be that sample in a single bottle submitted to the analytical laboratory.

4.3 The size of the sample must be sufficient to perform all analyses without the reuse of any portion of the sample. A 1000-mL sample should be sufficient.

5. Procedure for total acidity

5.1 *Scope*. This procedure covers the determination of the total acidity of 75% to 99% sulfuric acid. Three methods are given for weighing the specimens, namely, the Dely tube, the snake tube, and the weighing bottle methods.

5.2 *Summary of procedure*. A weighed specimen of acid is diluted in water and titrated with standardized 0.5M sodium hydroxide solution using phenolphthalein as the indicator.

5.3 *Interferences.* Acids other than sulfuric and compounds that consume sodium hydroxide will affect the accuracy of this method.

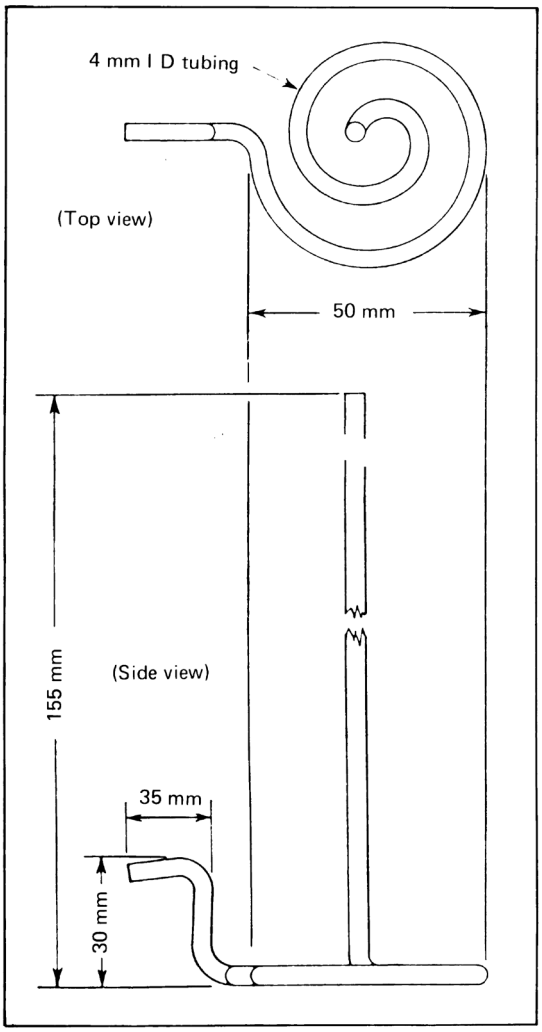

Fig. 1 Dely Tube

5.4 *Apparatus*

5.4.1 Dely tube (Fig. 1) or snake tube (Fig. 2)[1], or glass weighing bottle

5.4.2 Buret, 100-mL.

5.5 *Reagents*

5.5.1 *Phenolphthalein indicator*, alcoholic solution (10 g per 1000 mL).

5.5.2 *Sodium hydroxide*, standard solution, 0.5*M* NaOH (see TAPPI T 610 "Preparation of Indicators and Standard Solutions").

5.5.3 *Water* - Reagent Grade (ASTM Type I or II) water should be used to dilute the acid.

5.6 *Test specimen*. Table 1 shows the suggested specimen size range for a given acid strength.

[1] Names of suppliers of testing equipment and materials for this method may be found on the Test Equipment Suppliers list in the set of TAPPI Test Methods, or may be available from the TAPPI Technical Services Department.

Table 1. Specimen size for total acidity

H_2SO_4 %	Specimen size, g
98	1.9 to 2.2
94	2.0 to 2.3
90	2.1 to 2.4
85	2.2 to 2.6
80	2.3 to 2.7
77	2.4 to 2.8
75	2.5 to 2.9

5.7 *Test procedure*

5.7.1 Dely tube method. Invert the sample bottle several times. (Hold stopper in tight.) Insert the long arm of a dry, weighed Dely tube and withdraw by suction a convenient size specimen depending on the acid strength as given in Table 1. Invert the Dely tube and wipe the acid from the long arm with disposable tissue. Reweigh to the nearest 0.001 g and record the weight of the specimen. Incline the tube so that the acid runs back nearly to the bend of the short arm. Attach the short arm to an elevated water reservoir by means of a rubber tube closed near the glass beaker containing approximately 100 mL of water. Open the pinch clamp and flush the specimen into the beaker. Continue the flow of water until all acid is washed from the Dely tube.

NOTE 1: The Dely tube can be marked at points equivalent to weights given in Table 1.

NOTE 2: The presence of acid in the Dely tube may be detected by coloring the water in the reservoir with phenolphthalein indicator and the minimum amount of dilute NaOH solution that will produce a slight pink. The water flowing through the tube is decolorized as long as acid is present, and the appearance of a pink color indicates the absence of acid.

NOTE 3: The acid and water are separated by a bubble of air. This prevents the acid and water from mixing within the confines of the tube (the reaction of water plus acid causes heat - this should not occur in the tube).

Wash the long end of the Dely tube, collecting the washings in the beaker. Add 3 to 5 drops of phenolphthalein indicator solution. Record the temperature of the 0.5*M* NaOH solution, and then titrate the specimen to a pink end point. Record the titration to the nearest 0.02 mL.

5.7.2 *Snake tube method*. Invert the sample bottle several times. (Hold stopper in tight.) Insert the capillary end of a dry, weighed snake tube and withdraw by suction a convenient size specimen depending upon the acid strength as given in Table 1. Invert the tube so that the double bend is in a horizontal position. Wipe the acid from the capillary with disposable tissue. Reweigh to the nearest 0.001 g and record the weight of the specimen. Submerge the capillary of the tube in approximately 100 mL of water contained in the 400-mL beaker. Force the weighed specimen from the tube by a stream of water from a wash bottle by placing the delivery tip in the exposed end of the snake tube. Wash the tube with 50 to 70 mL of water. Remove the tube and wash the inside and outside free of acid. Swirl the contents

of the beaker gently while washing. Accumulate all washings in the beaker and add 3 to 5 drops of phenolphthalein indicator solution. Record the temperature of the 0.5*M* NaOH solution, and then titrate the specimen to a pink end point. Record the titration to the nearest 0.02 mL.

NOTE 4: Do not introduce the water into the snake tube too rapidly, as this will cause spattering.

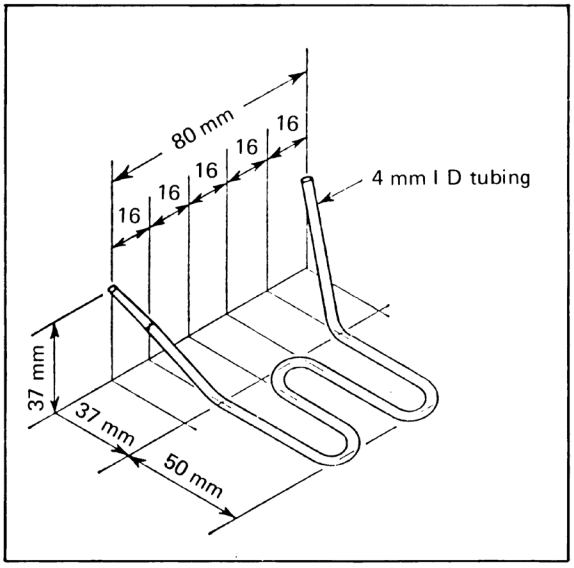

Fig. 2 Snake tube

5.7.3 *The weighing bottle method.* Weigh a dry stoppered weighing bottle and introduce a convenient size specimen depending upon the acid strength as given in Table 1. Reweigh to the nearest 0.001 g and transfer the specimen to a 400-mL beaker. Approximately 20 mLs of water should be in the beaker. Rinse the weighing bottle well with water, mixing well after the acid sample is first added, into the beaker to a total volume of 150 to 170 mL. Add 3 to 5 drops phenolphthalein indicator solution. Record the temperature of the 0.5*M* NaOH solution and then titrate the sample to a pink end point. Record the titration to the nearest 0.02 mL.

5.8 *Calculations*

5.8.1 Correct the buret reading for calibration errors and record as *V* the corrected delivered volume at the recorded temperature.

5.8.2 Calculate the total acidity as percentage of sulfuric acid as follows:

$$\text{Sulfuric acid, \%} = \frac{VN \times 0.04904 \times 100}{W}$$

where:

V = NaOH solution required for titration of the specimen, corrected mL

N = normality of the NaOH solution

W = amount of specimen used, g

5.9 *Report*. Report as a test result the average of duplicate determinations in percentage of sulfuric acid to the nearest 0.01%.

5.10 *Precision*

5.10.1 Repeatability (within a laboratory) = 0.29% abs.

5.10.2 Reproducibility (between laboratories) = 0.39% abs.; in accordance with the definition of these terms in TAPPI T 1200 "Interlaboratory Evaluation of Test Methods to Determine TAPPI Repeatability and Reproducibility."

5.10.3 These values are based on interlaboratory study on three samples containing 80%, 90%, and 95% sulfuric acid. Duplicate determinations were performed by one analyst in each of ten laboratories on alternate days.

6. Baumé gravity

6.1 *Scope*. This procedure describes the determination of the Baumé gravity of concentrated sulfuric acid by means of a glass hydrometer in the range from 57° to 66.3° Baumé. The Baumé gravity is determined at 15.5°C (60°F). This method is not applicable to readings above 66.2 Baumé gravity units.

6.2 *Summary of procedure.* A specimen of sulfuric acid is placed in a hydrometer cylinder, and when the temperature is constant, the Baumé gravity is read from the hydrometer scale.

6.3 *Significance*. The Baumé gravity is used to classify various grades of sulfuric acid. This method is not applicable for accurate determination of the concentration of sulfuric acid.

6.4 *Definition*. Baumé gravity (Bé) is defined by the following equation:

$$°\text{Bé} = 145 - \frac{145}{\text{sp gr } 15.5^{\circ}/15.5^{\circ}\text{C}}$$

or

$$145 - \frac{145}{\text{sp gr } 60^{\circ}/60^{\circ}\text{F}}$$

6.5 *Apparatus*

6.5.1 *Hydrometer*[1], streamline or torpedo design, precision grade for liquids heavier than water in ranges

from 57° to 62° Bé. The total length is approximately 305 mm (12 in.) divided to 0.05° Bé over a 152-mm (6-in.) (approximate) scale and standardized at 15.5°/15.5°C (60°/60°F) with a tolerance of 0.05° throughout. The modulus is:

$$\text{Bé} = 145 - \frac{145}{\text{sp gr } 15.5^{\circ}/15.5^{\circ}\text{C}}$$

or

$$145 - \frac{145}{\text{sp gr } 60^{\circ}/60^{\circ}\text{F}}$$

Each of the hydrometers must show on the scale the modulus (or formula) and 66° Bé = sp gr 1.8354 at 15.5°C (60°/60°F); 1 mL of water at 15.5° weighs 0.9990 g (1 ft^3 of water at 60°F weighs 62.37 lb avoirdupois).

6.5.2 *Thermometer*, having a range from -2° to +80°C (30° to 180°F) and conforming to the requirements for thermometer 15°C (60°F) as prescribed in ASTM Specifications E1.

6.5.3 *Cylinder, hydrometer*, glass, with or without lip, diameter 38 to 40 mm, height 325 to 375 mm.

6.6 *Temperature of test*. Baumé gravity is determined at 15.5° ± 0.3°C (60° ± 0.5°F).

6.7 *Test procedure*. Rinse a clean hydrometer cylinder with a portion of the acid to be tested, add a specimen, and adjust the temperature to 15.5° ± 0.3°C (60° ± 0.5°F) by external heating or cooling at cylinder. Place the cylinder in a vertical position in a location free of air currents. Insert the hydrometer in the specimen. Read the hydrometer when it has come to rest, floating freely, and the temperature is 15.5°C (60°F). The correct reading is that point on the hydrometer scale at which the surface of the liquid cuts the scale. Determine this point by placing the eye slightly below the level of the liquid and slowly raising it until the surface, first seen as a distorted ellipse, appears to become a straight line cutting the hydrometer scale.

6.8 *Calculation*. Calculate the specific gravity for later calculations according to the following formula:

$$\text{sp gr} = \frac{145}{145 - \text{°Bé}}$$

6.9 *Report.* From the average of duplicate determinations, report as a test result the Baumé gravity to the nearest 0.01 unit.

6.10 *Precision*

6.10.1 Repeatability (within a laboratory) = 0.04 units abs.;

6.10.2 Reproducibility (between laboratories) = 0.17 units abs.;

6.10.3 The above values are based on an interlaboratory study of three samples having Baumé gravities of approximately 61, 65, and 66 units. Duplicate analyses were performed by one analyst in each of nine laboratories on alternate days.

7. Nonvolatile matter

7.1 *Scope*. This procedure describes the gravimetric determination of nonvolatile matter in sulfuric acid. The lower limit of determination of nonvolatile matter is 0.001%.

7.2 *Summary of procedure.* A weighed specimen of acid is evaporated, ignited, and the residue weighed.

7.3 *Apparatus*

7.3.1 *Evaporating dish*, platinum or high-silica glass, 150 mL.

7.3.2 *Muffle furnace*, maintained at 800 ± 25°C (1472 ± 45°F).

7.3.3 *Crucible tongs*

7.4 *Procedure*

7.4.1 Clean a platinum or a high-silica glass dish.

NOTE 5: New platinum or high-silica glass dishes should be boiled in HCl (1:1) for 10 min, washed, and ignited in the muffle furnace for at least 1 h before their first use.

NOTE 6: High-silica glass dishes should be used only for low nonvolatile material. The residue remaining from specimens containing large amounts of nonvolatile matter may fuse into the dish.

Ignite in a muffle furnace at 800 ± 25°C (1472 ± 45°F) for at least 10 min. Cool in a desiccator to room temperature and weigh the dish to the nearest 0.1 mg.

NOTE 7: High-silica glass dishes should be allowed to cool at least 45 min before weighing.

7.4.2 Mix the sample by inverting the sample bottle until all solids are in suspension.

NOTE 8: It is important that the sample be well mixed and that all solids are in homogenous suspension so that a representative specimen can be obtained.

7.4.3 Transfer a weighed specimen containing a minimum of 50 g, weighed to the nearest 0.1 g, or a weighed specimen of sufficient size to yield not less than 1 mg of residue to the evaporating dish and evaporate to dryness over a burner or hot plate in a hood. After evaporation, ignite the residue in the muffle furnace for 10 min. Use crucible tongs in handling the evaporating dish at all times.

7.4.4 Allow the dish to cool to room temperature in a desiccator and rapidly weigh the specimen dish to the nearest 0.1 mg.

7.5 *Calculation*. Calculate the percentage of nonvolatile matter as follows:

$$\text{Nonvolatile matter, \%} = \frac{R - D}{W} \times 100$$

where:

R = weight of evaporating dish and residue, g

D = weight of evaporating dish, g

W = amount of specimen used, g

7.6 *Report*. Report as a test result the average of duplicate determinations in percentage of nonvolatile matter to the nearest 0.0001%. If this value is less than 0.0010%, report as “less than 0.0010%.”

7.7 *Precision*

7.7.1 Repeatability (within a laboratory) = 0.0019% abs.;

7.7.2 Reproducibility (between laboratories) = 0.0033% abs.; in accordance with the definitions of these terms in TAPPI T 1200.

7.7.3 The above values are based on an interlaboratory study of five samples, containing approximately 0.003, 0.005, 0.010, 0.014, and 0.024% nonvolatile matter. Duplicate determinations were performed by one analyst in each of eight laboratories on alternate days.

8. Iron

8.1 *Scope*. This procedure is a colorimetric estimation of iron in sulfuric acid. The lower limit of determination of iron is 0.0001%.

8.2 *Summary of procedure.* The iron is reduced and determined colorimetrically with 1, 10-phenanthroline (orthophenanthroline), which forms an orange-red complex with ferrous iron. The intensity of the color so formed is measured in a photometer calibrated with standard iron solution.

8.3 *Interferences.* It is beyond the scope of this method to describe procedures for overcoming all possible interferences that may be encountered. Chromium interferes if it is present in sufficient quantity for the color of chromic or chromate ion to have masking effect. Copper, antimony, cobalt, mercury (I), and tin (II, IV) interfere in

concentrations of 10 to 50 ppm. Cadmium, mercury (II), zinc, and nickel complexes may interfere but can be overcome by the use of excess of the 1, 10-phenanthroline reagent.

8.4 *Apparatus*

8.4.1 Photometer, any photoelectric spectrophotometer or filter photometer that will measure the absorbance of the solutions in the range from 500 to 525 nm.

8.4.2 *Absorption cells*, 20-mm light path.

NOTE 9: This procedure has been written for a cell having a 20-mm light path. Cells having other dimensions may be used, provided suitable adjustments can be made in the amounts of specimen and reagents used.

8.5 *Reagents*

8.5.1 *Ammonium acetate*, acetic acid solution.

8.5.2 *Ammonium hydroxide solution (1:1).*

8.5.3 *Congo red paper*

8.5.4 *Hydroxylamine hydrochloride solution (100 g per 1000 mL*).

8.5.5 *Iron,* standard solution (1 mL = 0.01 mg Fe). Dissolve 0.1000 g of iron in 10 mL of hydrochloric acid (HCl, 1:1) and 1 mL of bromine water. Boil until the excess bromine is removed. Add 200 mL of HCl, cool, and dilute to 1000 mL in a volumetric flask. Dilute 100 mL of this solution to 1000 mL.

8.5.6 *1, 10-phenanthroline monohydrate*, 3 g per 1000 mL.

8.5.7 *Water*, Reagent Grade (ASTM Type I or II) or equivalent.

8.6 *Calibration*

8.6.1 To a series of 100-mL volumetric flasks, pipet 0, 2, 4, 8, and 10 mL of standard iron solution. To each flask add the following reagents in order, mixing after addition of each: 20 mL of water, 1 mL of hydroxylamine hydrochloride solution, 5 mL of 1,10-phenanthroline solution, and NH_4OH (1:1) as required to bring the pH to 3.5 to 4.0 (just alkaline to congo red paper). Add 5 mL of ammonium acetate solution, dilute to the mark with water, mix thoroughly, and allow to stand approximately 15 min.

8.6.2 Measure the absorbances of the solution using a photometer with a wavelength setting of 510 nm or a filter photometer equipped with a filter in the range from 500 to 525 nm adjusting the photometer to read zero absorbency for the reagent blank.

8.6.3 Plot on coordinate paper the absorbances of the calibration solutions against milligrams of iron present per 100 mL of solution.

8.7 *Test procedure*

8.7.1 Mix the sample by inverting the sample bottle until all solids are in suspension (refer to Note 8).

8.7.2 Insert a 70-mm stem funnel in a 100-mL volumetric flask and add 50 mL of water.

NOTE 10: This is done to keep the neck of the flask dry and prevent spitting or spattering on introducing the specimen.

8.7.3 Remove the funnel and slowly add, with continual swirling of the contents of the flask, 1 g of specimen weighed by difference to the nearest 0.001 g. Wash down the neck of the flask with a small stream (approximately 5

mL) of water.

8.7.4 Add to the flask the following reagents in order, mixing after addition of each: 1 mL of hydroxylamine hydrochloride solution, 5 mL of 1,10-phenanthroline solution, and NH_4OH (1:1) as required to bring the pH of the solution to 3.5 to 4.0 (just alkaline to congo red paper). Add 5 mL of ammonium acetate solution, dilute to the mark with water, mix thoroughly, and allow to stand approximately 15 min.

8.7.5 Prepare a blank solution using all reagents but omitting the specimen. Allow both solutions to stand about 15 min.

8.7.6 Determine the absorbance of the specimen at the same wavelength used for the calibration curve, blanking the instrument at zero absorbance with the blank solution. Determine from the calibration curve the milligrams of iron that correspond to the observed absorbance.

NOTE 11: If the color obtained is too intense to fall within the range of the calibration curve, repeat with a smaller specimen and make appropriate calculations based on this smaller specimen.

NOTE 12: If the color obtained is less than that obtained with 0.01 mg of Fe, repeat 7.7.3 as follows: Transfer 10 g of specimen, weighed by difference to the nearest 0.01 g, to a 50-mL beaker and evaporate to almost dryness over a burner or hot plate in a hood. Add 10 mL of water and 2 mL of HCl (sp gr 1.19) and heat to dissolve any solids. Transfer the solution to a 100-mL volumetric flask with a minimum amount of water and proceed in accordance with 7.7.4.

8.8 *Calculation*. Calculate the percentage of iron as follows:

$$\text{Iron, \%} = \frac{M}{W \times 1000}$$

where:

M = amount of iron found from calibration curve, mg

W = amount of specimen used, g

8.9 *Report*. Report as a test result the average of duplicate determinations in percentage of iron to the nearest 0.0001%. If this value is less than 0.0001%, report as “less than 0.0001%.”

8.10 *Precision*

8.10.1 Repeatability (within a laboratory) = 0.0005% abs.;

8.10.2 Reproducibility (between laboratories) 0.0009% abs.; in accordance with the definition of these terms in TAPPI T 1200.

8.10.3 The above values are based on an interlaboratory study of three samples containing approximately 0.004, 0.005, and 0.008% iron. Duplicate analyses were performed by one analyst in each of nine laboratories on alternate days.

9. Sulfur dioxide

9.1 *Scope*. This procedure describes the determination of free sulfur dioxide dissolved in sulfuric acid.

9.2 *Summary*. The sulfur dioxide content is determined on the basis of the consumption of standard iodine solution. The method assumes that sulfur dioxide is the only compound present which will consume iodine.

9.3 *Reagents*

9.3.1 *Standard iodine solution*, 0.005*M* (0.01*N*).

9.3.2 *Starch indicator solution*, 10 g/1000 mL.

9.4 *Test procedure*

9.4.1 While stirring slowly, add a 100-mL specimen, measured in a graduate, to 500 mL of cold distilled water in a 1000-mL beaker. Keep the mixture cooled in an ice water bath during the addition.

9.4.2 Add 10 mL of freshly prepared starch indicator solution and titrate immediately with standard iodine solution to the first appearance of a blue color throughout the solution.

9.4.3 Similarly titrate a blank using 100 mL of diluted reagent grade sulfuric acid, which has been diluted with distilled water to approximately the same specific gravity as the specimen.

9.5 *Calculation*. Calculate the percentage of sulfur dioxide as follows:

$$\text{Sulfur dioxide, \%} = \frac{(A - B) \times M \times 6.4066}{\text{mL of specimen} \times \text{sp gr}}$$

where:

A = iodine solution required for the titration of the specimen, mL

B = iodine solution required for the titration of the blank, mL

M = molarity of the iodine solution

9.6 *Report.* Report as a test result the average of duplicate determinations in percentage of sulfur dioxide to the nearest 0.001%. If this value is less than 0.002%, report as “less than 0.002%.”

10. Arsenic

10.1 *Scope.* This procedure describes a colorimetric determination of arsenic in sulfuric acid. The lower limit of determination is 0.01 ppm of arsenic.

10.2 *Summary of procedure*. The arsenic is reduced to arsine gas (AsH_3), which is absorbed in a pyridine solution of silver diethyldithiocarbamate, forming a red-colored complex, the intensity of which is measured on a photometer calibrated with standard arsenic solution.

CAUTION: Inorganic arsenic compounds are listed as known carcinogens by IARC (International Agency for Research on Cancer), NTP (National Toxicology Program) and OSHA (Occupational Safety & Health Administration). Proper laboratory technique and engineering controls (i.e. ventilation) must be used to insure that there is no exposure to arsine gas generated by this procedure.

10.3 *Interference*. Antimony is reduced to stibine which reacts with the reagent. The color produced is slightly different from that produced by arsine.

10.4 *Apparatus*

10.4.1 *Absorption cells*, 20-mm light path.

NOTE 13: This procedure has been written for a cell having a 20-mm light path. Cells having other dimensions may be used, provided suitable adjustments can be made in the amounts of sample and reagents used.

10.4.2 *Arsine generator* (Fig. 3)[1]

10.4.3 *Flasks*, volumetric, ground-glass stoppered, 10 mL.

10.4.4 *Photometer*, any photoelectric spectrophotometer or filter photometer that will measure the absorbance of the solutions in the range from 500 to 575 nm.

10.5 *Reagents*

NOTE 14: All reagents and water used in the determination of arsenic by this method should be very low in arsenic, particularly the zinc. If the $NaNO_3$ is high in arsenic, substitute 5 drops of HNO_3 (sp gr 1.42) for the 0.1 g of $NaNO_3$.

10.5.1 *Arsenic*, standard solution (1 mL = 0.001 mg As). Dissolve 0.1320 g of arsenic trioxide (As_2O_3) in 10 mL of sodium hydroxide solution (NaOH, 100 g/1000 mL), neutralize with sulfuric acid (H_2SO_4, 1:15), add 10 mL of the acid in excess, and dilute with water to 1000 mL. To 10 mL of this solution (1 mL = 0.1 mg As) add 10 mL of H_2SO_4 (1:15), and dilute with water to 1000 mL.

10.5.2 *Hydrochloric acid* (sp gr 1.189), concentrated hydrochloric acid (HCl).

10.5.3 *Lead acetate impregnated glass wool*. Dissolve 100 g of lead acetate trihydrate ($Pb(C_2H_3O_2)_2 \cdot 3H_2O$) in 200 mL of water. Saturate glass wool with the solution, remove excess solution and vacuum dry at room temperature. Store the impregnated wool in a capped bottle.

10.5.4 *Methyl red indicator solution* (5 g/1000 mL).

10.5.5 *Potassium iodide solution* (100 g/1000 mL).

10.5.6 *Pyridine* (C_5H_5N). This reagent must be water white.

10.5.7 *Silver diethyldithiocarbamate* [$(C_2H_5)_2$ NSCSAg] solution (5 g/1000 mL of pyridine). Dissolve 1 g in200 mL of pyridine. Store in amber bottle. Prepare fresh monthly.

10.5.8 *Sodium chloride* (NaCl).

10.5.9 *Sodium hydroxide solution* (100 g/1000 mL). Dissolve 100 g of sodium hydroxide (NaOH) in water and dilute to 1000 mL with water.

10.5.10 *Sodium nitrate* ($NaNO_3$).

10.5.11 *Stannous chloride solution* ($SnCl_2 \cdot 2H_2O$) (400 g/1000 mL). Dissolve 40 g of stannous chloride dihydrate ($SnCl_2 \cdot 2H_2O$) in a mixture of 25 mL of water and 75 mL of HCl (sp gr 1.19).

10.5.12 *Zinc*, 20 mesh.

10.6 *Calibration*

10.6.1 Into a series of the 125-mL generator flasks pipet 0, 1, 3, 5, 10, and 15 mL of standard arsenic solution.

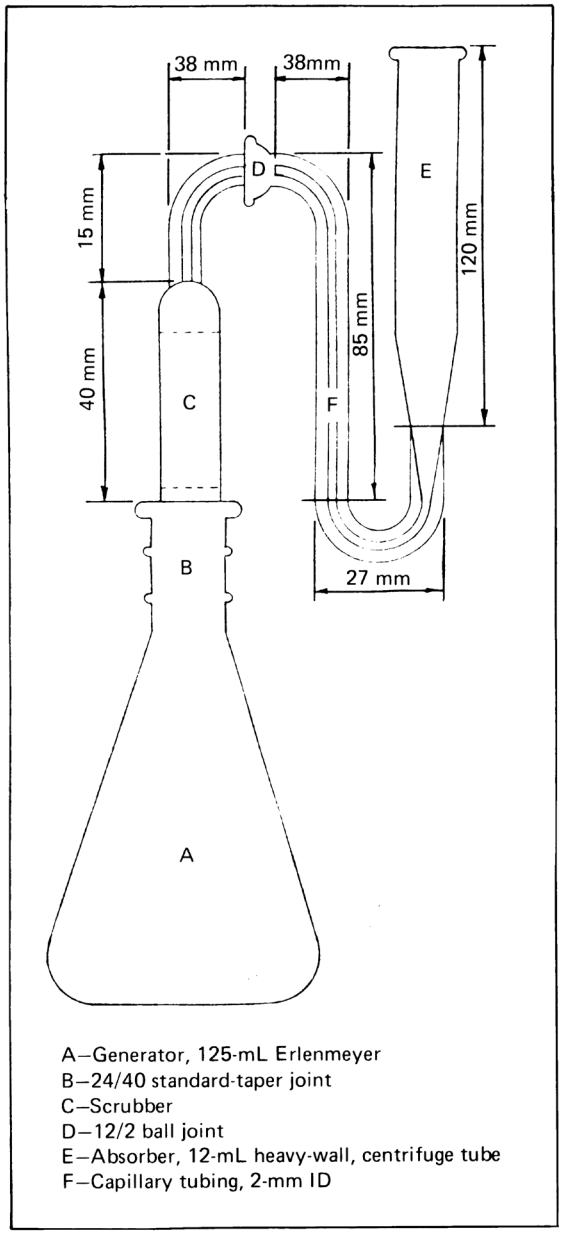

Fig. 3. Arsine generator.

NOTE 15: All new glassware must be cleaned with hot concentrated H_2SO_4, rinsed with water, rinsed with acetone, and dried. If the glassware is reserved for arsenic determinations exclusively, the H_2SO_4 may be omitted in subsequent washings.

10.6.2 Dilute each flask to 35 mL with water. Add 5 mL of HCl, 2 mL of KI solution, and 8 drops of $SnCl_2$ solution.

NOTE 16: Too great an excess of $SnCl_2$ causes loss of arsenic by reducing it to elemental arsenic.

10.6.3 Mix the solutions and allow them to stand for 15 min to ensure complete reduction of the arsenic to the trivalent form.

10.6.4 Pack the scrubber tube for each flask with the lead acetate impregnated glass wool and moisten with 1 drop of lead acetate solution. Lubricate the standard taper and ball-and-socket joints with lubricant[1] and assemble the scrubber-absorber unit. Do not attach scrubber-absorber unit to generator flask. Pipet 3 mL of the silver diethyldithiocarbamate solution into each absorber section. By means of a powder funnel, add quickly 3.0 g of zinc to each flask. Immediately attach the scrubber-absorber unit to the generator flask and let stand for 30 min.

10.6.5 Transfer the solutions from the absorber sections to separate dry 10-mL volumetric flasks. Rinse out each absorber section with pyridine and transfer the washings to the same flask. Make up to volume with pyridine and mix.

10.6.6 Measure the absorbances of the solutions using a photometer with a wavelength setting of 560 nm or a filter photometer equipped with a filter in the range from 500 to 575 nm, adjusting the photometer to read zero absorbance for the reagent blank.

10.6.7 Plot on coordinate paper the absorbances of the calibration solutions against milligrams of arsenic present per 10 mL.

10.7 *Test procedure*

10.7.1 From a graduated cylinder, transfer about a 50-mL specimen to a 100-mL beaker. Record the number of mL taken, *W*. Add about 0.1 g of $NaNO_3$ and 0.1 g of NaCl and evaporate on a hot plate in the hood to almost dryness.

10.7.2 Wash the specimen into a generator flask with small portions of water. Do not exceed 30 mL total volume.

10.7.3 Add 1 drop of methyl red indicator solution and add NaOH solution dropwise until the solution is just alkaline (yellow). Dilute to 35 mL with water.

10.7.4 Add 5 mL of HCl, 2 mL of KI solution, and 8 drops of $SnCl_2$ solution. Mix the solution and allow it to stand for 15 min.

10.7.5 Pack the scrubber tube for the flask with the lead acetate impregnated glass wool and moisten with 1 drop of lead acetate solution. Lubricate the standard taper and ball-and-socket joints with lubricant and assemble the scrubber-absorber unit. Do not attach scrubber-absorber unit to generator flask. Pipet 3 mL of the silver diethyldithiocarbamate solution into the absorber section. By means of a powder funnel, add quickly 3.0 g of zinc to the flask. Immediately attach the scrubber-absorber unit to the generator flask and let stand for 30 min.

10.7.6 Transfer the solution from the absorber section to a dry 10-mL volumetric flask. Rinse out the absorber section with pyridine and transfer the washings to the same flask. Make to volume with pyridine and mix.

10.7.7 Prepare a blank solution using all reagents but omitting the specimen.

10.7.8 Determine the absorbance of the specimen at the same wavelength used for the calibration curve, blanking the instrument at zero percent absorbance with the blank solution. Determine from the calibration curve the milligrams of arsenic that correspond to the observed absorbance.

NOTE 17: If the color obtained is too intense to fall within the range of the calibration curve, repeat with a smaller specimen.

10.8 *Calculation*. Calculate the parts per million arsenic as follows:

$$\text{Arsenic, ppm} = \frac{M \times 1000}{W \times \text{sp gr}}$$

where:

M = arsenic found from calibration curve, mg

W = amount of specimen, mL

10.9 *Report.* Report as a test result the average of duplicate determinations in parts per million of arsenic to the nearest 0.01 ppm. If this value is less than 0.01 ppm, report as "less than 0.01 ppm."

10.10 *Precision*

10.10.1 Repeatability = 0.014 abs. (at 0.06 ppm); 0.08 abs. (at 0.60 ppm).

10.10.2 Reproducibility = 0.05 abs. (at 0.06 ppm); 0.37 abs. (at 0.60 ppm); in accordance with the definitions of these terms in TAPPI T 1200.

10.10.3 The above values are based on an interlaboratory study of two samples containing approximately 0.06 and 0.60 ppm of arsenic. Duplicate analyses were performed by one analyst in each of eight laboratories on alternate days.

11. Keywords

Sulfuric acid, Acidity, Iron, Sulfur dioxide, Arsenic, Volatility, Density

12. Additional information

12.1 Effective date of issue: to be assigned

12.2 Related method: ASTM E 223 (technically identical).

12.3 This method was reclassified to a classical method in 1997.

Your comments and suggestions on this procedure are earnestly requested and should be sent to the TAPPI Standards Department. ■