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T \_\_\_\_\_ 611 \_\_\_\_\_

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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 bleaching powder, calcium hypochlorite  
bleach liquor, and bleach sludge  
(REAFFIRMATION of Classical Method T 611 cm-07)  
(No changes from previous drafts: Standard reaffirmed)**

**1. Scope and significance**

1.1 This method describes the procedure for determining the "available chlorine" of bleaching powder, calcium hypochlorite bleach liquor, and bleach sludge. In addition, the procedures for determining total chlorine and titratable alkali are described. In these procedures the available chlorine, as determined, includes any chlorite that may be present.

1.2 Available chlorine is determined by adding a measured amount of sample solution to an acidified solution of potassium iodide, liberating an equivalent amount of iodine. This free iodine is determined by titration with standardized sodium thiosulfate solution, using a starch indicator endpoint.

1.2.1 Total chlorine is determined titrimetrically by the Mohr method, employing standardized neutral silver

nitrate solution. The determination involves treatment of a measured amount of sample solution with an excess of dilute (3%) hydrogen peroxide to reduce hypochlorites to chloride. The determination includes chloride formed during manufacture of the bleach as well as that formed through the reduction treatment. Potassium chromate is employed as indicator in the titration.

1.2.2 Titratable alkali is determined in a measured amount of the sample solution with standardized hydrochloric acid solution. Bleaching properties of the sample are discharged by the addition of small amounts of hydrogen peroxide (3%). Methyl orange/xylene cyanole indicator is used as the endpoint detector.

## 2. Definitions

2.1 *Available chlorine* (in chlorine bleaching), chlorine present as hypochlorite, chlorite, chlorine dioxide, or elemental chlorine, expressed in terms of elemental chlorine of the *equivalent oxidizing* power. Because one molecule of hypochlorite is equivalent in oxidizing power to two atoms of chlorine, its *available* chlorine is twice its total chlorine. Consequently, the chloride content (as Cl) of a sample of bleach is the difference between the total chlorine content and one-half the available chlorine (disregarding any chlorate that may be present).

## 3. Bleaching powder analysis

### 3.1 *Apparatus*

3.1.1 *Tubular sampler*, or “trier” about 300 mm (12 in.) long, 12 mm (½ in.) wide, with a concavity of 6 mm (¼ in.).

3.1.2 *Weighing bottle*, glass-stoppered.

3.1.3 *Mortar and pestle*

3.1.4 *Glassware*: volumetric flask, 1000 mL; pipet, with wide orifice, 50 mL; graduated cylinder, 10 mL; Erlenmeyer flask, 250 mL; buret, 50 mL; jar, about 1 L capacity, with a tightly fitting lid.

3.2 *Reagents*. For dilutions, use distilled water which has been boiled recently and cooled.

3.2.1 *Potassium iodide*, 20% solution of KI.

3.2.2 *Acetic acid*, 20% solution of CH<sub>3</sub>COOH.

3.2.3 *Sodium thiosulfate*, 0.1N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (see TAPPI T 610 “Preparation of Indicators and Analytical Reagents, and Standardization of Volumetric Solutions”).

3.2.4 *Starch indicator*. See TAPPI T 610.

3.3 *Sampling and test specimen*

3.3.1 Sample at least 1% of the drums or five drums, whichever is larger.

3.3.2 Insert the trier through an opening at the center of the side of each drum three times. The position of the trier upon the first insertion is to be toward the top of the drum, the second, horizontally, and the third toward the bottom. Quickly and thoroughly mix the sample thus drawn; cone and quarter as described in T 605 “Reducing a Gross Sample of Granular or Aggregate Material to Testing Size” until reduced to an amount sufficient to fill the jar.

Keep the jar tightly closed except when withdrawing portions for analysis. Store in a cool, dark place until the tests are completed.

3.3.3 Discard the outside, top layer of the sample in the storage jar to a depth of about 20 mm (3/4 in.), then quickly and thoroughly mix the rest of the sample and place a portion in a glass-stoppered weighing bottle. Keep the bottle covered while in the balance case, as chlorine is very corrosive.

3.3.4 Weigh to two decimal places a test specimen of about 8 g from the weighing bottle into the mortar.

#### 3.4 Procedure

3.4.1 Add a little water to the specimen and with the pestle, triturate to a smooth cream. Stir in more water, let it settle for a few moments, then pour off the supernatant liquid through a funnel into a 1000-mL volumetric flask about two thirds full of distilled water. Repeat the trituration and dilution of any sediment remaining in the mortar until the entire specimen is conveyed without loss to the flask. Conduct the entire operation as rapidly as possible to minimize loss of chlorine.

3.4.2 Fill the flask to the mark with distilled water, mix well, and immediately pipet a 50-mL aliquot into the 250-mL Erlenmeyer flask, without allowing the material to settle. Add 10 mL of 20% KI solution, mix by swirling, or with a magnetic stirrer and add 10 mL of 20% CH<sub>3</sub>COOH. Mix again and titrate immediately with the standardized 0.1N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution until the iodine color is almost discharged. Add 1 mL of starch indicator solution and continue the titration to the disappearance of the blue color.

#### 3.5 Calculation

$$\text{Available chlorine, \%} = \frac{V \times A \times 35.46 \times 100}{50B}$$

where:

$V$  = volume of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, mL

$A$  = normality of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>

$B$  = weight of specimen, g

3.6 *Report.* Report the result as the percentage of available chlorine, based on the original weight of bleaching powder to the nearest 0.1.

**NOTE 1:** Usually for bleaching powder only the percentage of available chlorine is required. However, if desired, the liquid may be analyzed also for total chlorine (see 4.5) and titratable alkali (see 4.6), both as in bleach liquor.

## 4. Bleach liquor analysis

### 4.1 Apparatus

4.1.1 *Spot plate*

4.1.2 *Glassware:* volumetric flask, 250 mL; pipets, 1, 25, and 50 mL; Erlenmeyer flask, 250 mL; graduated cylinder, 10 mL; buret, 50 mL; beaker, 400 mL; brown bottle, approximately 500 mL; glass rod.

4.2 *Reagents,* same as specified in 3.2, and in addition:

4.2.1 *Hydrogen peroxide,* 3% solution of H<sub>2</sub>O<sub>2</sub>, both unadjusted and neutral.

4.2.2 *Nitric acid,* concentrated HNO<sub>3</sub> (sp gr 1.42).

4.2.3 *Calcium carbonate,* powdered CaCO<sub>3</sub>, chloride free.

4.2.4 *Potassium chromate indicator,* 2.5% K<sub>2</sub>CrO<sub>4</sub>.

4.2.5 *Standardized 0.1N AgNO<sub>3</sub>,* neutral solution. See TAPPI T 610, store in a dark bottle.

4.2.6 *Starch-indicator.* See TAPPI T 610 "Preparation of Indicators and Standard Solutions."

4.2.7 *Standardized 0.1N HCl* (see TAPPI T 610).

4.2.8 *Standardized 0.1N NaOH* (see TAPPI T 610).

4.2.9 *Methyl orange indicator* (see TAPPI T 610) or methyl orange/xylene cyanole (available commercially from chemical supply companies), which changes from green in an alkali to dark red in an acid, with the end point of metallic gray for the analysis in this method.

4.3 *Sampling.* Agitate the batch thoroughly and withdraw a sample of approximately 500 mL of the liquor. Store in a dark bottle away from light and heat, and analyze as soon as possible.

4.4 *Procedure for available chlorine*

4.4.1 Thoroughly agitate the sample in the dark bottle, pipet a 50-mL test specimen into a 250-mL volumetric flask, and dilute to the mark with water. Pipet a 25-mL aliquot portion into approximately 25 mL of water contained in a 250-mL Erlenmeyer flask. Add 10 mL of 20% KI solution, mix by swirling, and acidify the suspension by adding 10 mL of 20% CH<sub>3</sub>COOH.

4.4.2 Mix the suspension again by swirling and titrate immediately with 0.1N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> until the iodine color is almost discharged; then add about 1 mL of the starch indicator and continue the titration to the disappearance of the blue color.

**NOTE 2:** If the specimen is strongly alkaline, the color of the end point may fade. If so, first neutralize most of the alkalinity with diluted HCl (1:1), then add 10 mL of 20% CH<sub>3</sub>COOH as specified.

4.4.3 *Calculation.* Calculate the available chlorine, in grams per liter, as follows:

$$V \times A \times 35.46$$

Available chlorine = \_\_\_\_\_

where:

$V$  = volume of  $\text{Na}_2\text{S}_2\text{O}_3$ , mL

$A$  = normality of  $\text{Na}_2\text{S}_2\text{O}_3$

4.4.4 *Report.* Report the result as grams of available chlorine per liter to three figures.

4.5 *Procedure for total chlorine*

4.5.1 Agitate the test specimen in the 250-mL volumetric flask (see 4.4.1) and pipet a 25-mL aliquot into a 250-mL Erlenmeyer flask. Add 3%  $\text{H}_2\text{O}_2$  solution until effervescence ceases, then add a few drops of concentrated  $\text{HNO}_3$ . Mix and add  $\text{CaCO}_3$  in slight excess of its dissolution.

**NOTE 3:** Add the  $\text{CaCO}_3$  in slight excess only. An off-color end point occurs if the pH is appreciably higher. The pH when the end point of the titration is reached should be approximately 8.

4.5.2 Add about 0.5 mL of  $\text{K}_2\text{CrO}_4$  indicator to the flask, boil gently until the lemon-yellow color is permanent, then cool to room temperature and titrate with standardized 0.1N neutral  $\text{AgNO}_3$  to a faint orange tint.

4.5.3 *Calculation.* Calculate the total chlorine, in grams per liter, as follows:

$$\text{Total chlorine} = \frac{V \times A \times 35.46}{5}$$

where:

$V$  = volume of  $\text{AgNO}_3$ , mL

$A$  = normality of  $\text{AgNO}_3$

4.5.4 *Report.* Report the result as grams of total chlorine per liter, to three figures.

4.6 *Procedure for titratable alkali*

4.6.1 Agitate the test specimen in the 250-mL volumetric flask (see 4.4.1) and pipet a 50-mL aliquot (equivalent to 10 mL of original sample solution) into a 400-mL beaker containing approximately 100 mL of distilled water. Add neutral 3%  $\text{H}_2\text{O}_2$  solution in 0.5-mL portions until a drop of the solution from the beaker no longer gives a blue reaction with starch-iodide solution on a spot plate. Add a few drops of the methyl orange or methyl orange/xylene cyanole indicator. Titrate the reacted solution to the end point (orange color) with 0.1N  $\text{HCl}$ , then add

5.00 mL of the acid in excess (permanent pink color). Record the total volume times normality as *A*.

4.6.2 Mix thoroughly and back titrate the excess HCl with 0.1*N* NaOH to the indicator end point (faint yellow color). Record the volume in milliliters times normality as *B*.

4.6.3 *Calculation*

$$\text{Titrateable alkali, g/L expressed as Ca(OH)}_2 = \frac{(A - B) \times 37.00}{10}$$

4.6.4 *Report.* Report the result as grams of titrateable alkali as Ca(OH)<sub>2</sub> per liter to three figures.

## 5. Bleach sludge analysis

5.1 *Apparatus*

5.1.1 *Mortar and pestle*

5.1.2 *Spot plate*

5.1.3 *Glassware:* volumetric flasks, 100 and 500 mL; funnel; pipet, 1 mL; pipet, wide-orifice, 25 and 50 mL; Erlenmeyer flask, 250 mL; buret, 50 mL; graduated cylinder, 10 mL; beaker, 400 mL; brown bottle, approximately 500 mL; glass rod.

5.2 *Reagents*

5.2.1 Reagents as specified in 3.2 and 4.2, except instead of 20% acetic acid solution, glacial CH<sub>3</sub>COOH is required.

5.3 *Sampling*

5.3.1 Agitate the sludge thoroughly and withdraw a sample of about 500 mL. Because sludge settles rapidly, take particular effort to obtain a representative sample.

**NOTE 4:** If the sludge is too thick to measure volumetrically with accuracy, dilute the sludge accurately to a known degree when taking the sample.

5.3.2 Store in a dark bottle, away from heat, and analyze as soon as possible.

5.3.3 Agitate the sample thoroughly, then quickly fill a 100-mL volumetric flask to the mark. Decant the liquid and suspended material into a 500-mL volumetric flask. Add all the settled residue, a little at a time, to the mortar and grind; dilute with distilled water and transfer the portions to the 500-mL flask without loss. Be sure that any lumps that might plug the orifice of the 25-mL pipet to be used are ground up. Finally complete the preparation of the test specimen by adding distilled water to the mark.

5.4 *Procedure for available chlorine*

5.4.1 Agitate the test specimen thoroughly and, with a wide-orifice pipet, measure a 25-mL aliquot into a 250-mL Erlenmeyer flask containing 25 mL of distilled water. Add 10 mL of 20% KI solution and 10 mL of glacial

acetic acid. Titrate the liberated iodine with 0.1N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> as in 4.4.1.

5.4.2 *Calculation.* Same as in 4.4.3. Apply a factor if the sludge has been diluted.

5.4.3 *Report.* See 4.4.4. Report as grams of available chlorine per liter of the original sludge.

5.5 *Procedure for total chlorine*

5.5.1 After agitation of the test specimen in the 500-mL volumetric flask (see 5.3.3), transfer another 25-mL aliquot into a 250-mL Erlenmeyer flask. Add 3% H<sub>2</sub>O<sub>2</sub> until effervescence ceases, then just sufficient concentrated HNO<sub>3</sub> to dissolve the acid-soluble components of the sludge with a few drops in excess. Add CaCO<sub>3</sub> in slight excess and a few drops of K<sub>2</sub>CrO<sub>4</sub> indicator. Proceed as in 4.5.2.

5.5.2 *Calculation.* Same as in 4.5.3. Apply a factor if the sludge is diluted.

5.5.3 *Report.* See 4.5.4. Report as grams of total chlorine per liter of the original sludge.

5.6 *Procedure for titratable alkali*

5.6.1 After agitation of the test specimen in the 500-mL volumetric flask (see 5.3.3), transfer a 50-mL aliquot to a 400-mL beaker containing approximately 100 mL of distilled water. Add neutral 3% H<sub>2</sub>O<sub>2</sub> solution in 0.5-mL portions until a drop of the contents of the beaker on a spot plate no longer gives an immediate blue reaction with starch-iodide solution. Stir well with a glass rod to release oxygen from the solution. Add a few drops of the methyl orange indicator, titrate with 0.1N HCl to a permanent pink color, and then add 10 mL of 0.1N HCl in excess. Record the total volume in milliliters times normality of HCl as A. Proceed as in 4.6.2.

5.6.2 *Calculation.* See 4.6.3. Apply a factor if the sludge has been diluted.

5.6.3 *Report.* See 4.6.4. Report in grams per liter of the original sludge.

## 6. Precision

6.1 *Repeatability* (within a laboratory). The following estimates of precision are based on limited experience in a single laboratory using triplicate samples:

6.1.1 Calcium hypochlorite bleach liquor: duplicate test results (each consisting of one test determination) may be expected to agree within the following values:

6.1.1.1 Available chlorine, 0.2 g/L

6.1.1.2 Total chlorine, 0.2 g/L

6.1.1.3 Titratable alkali, 0.03 g/L

6.1.2 Bleach sludge: repeatability is heavily dependent on sampling techniques due to the high solids content. With careful sampling, duplicate determinations may be expected to agree within the following values:

6.1.2.1 Available chlorine, 0.3 g/L

6.1.2.2 Total chlorine, 0.1 g/L

6.1.2.3 Titratable alkali, 0.6 g/L

6.2 *Reproducibility* (between laboratories): not known.

6.3 The above data were obtained in accordance with definitions of these terms in TAPPI T 1206

“Precision Statement for Test Methods.”

## 7. Keywords

Calcium hypochlorite, Bleach, Bleach liquor, Active chlorine, Titratable alkali, Chlorine sludge, Alkali

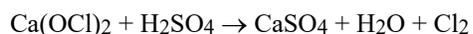
## 8. Additional information

8.1 Effective date of issue: to be assigned.

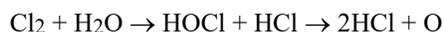
8.2 Bleaching powder is a complex combination of calcium hypochlorite ( $\text{Ca}(\text{OCl})_2$ ), calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) and water. Disregarding the  $\text{Ca}(\text{OH})_2$  and water, it is sometimes designated as “chloride of lime” ( $\text{CaOCl}_2$ ), a combination of one mole each of  $\text{Ca}(\text{OCl})_2$  and  $\text{CaCl}_2$  according to the reaction:



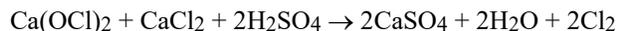
8.2.1 When bleaching powder is treated with acid, it produces “available chlorine” (which sets nascent oxygen free to produce the bleaching action) according to the reactions:



and



8.2.2 Considered in another way, one mole of hypochlorite and one mole of chloride produce two moles of “available” chlorine:



8.3 Bleach liquor may be made by dissolving bleaching powder in water, or by chlorinating milk of lime ( $\text{Ca}(\text{OH})_2$ ) according to the reaction:



In either case a small quantity of the total chlorine may be present as less desirable compounds, such as chlorate or excess (inactive) chloride.

8.4 Bleach sludge settles out in the commercial preparation of bleach liquor, because of excess  $\text{Ca}(\text{OH})_2$  and the insoluble components of the lime. This sludge is usually discarded, but a chemical analysis is frequently made to determine the amounts of chlorine and of lime in it. Some excess of  $\text{Ca}(\text{OH})_2$  may be present in the bleach liquor.

8.5 Titratable alkali includes mainly hydroxides and carbonates of Ca and Mg. If desired, titratable hydroxide alkali may be determined approximately as follows:

8.5.1 Pipet a 50-mL aliquot of the test sample from the 500-mL volumetric flask (see 5.3.3) into a 400-mL beaker containing approximately 100 mL of distilled water. Add neutral 3%  $\text{H}_2\text{O}_2$  in 0.5-mL portions until a drop of the contents of the beaker on a spot plate no longer gives a blue reaction with starch-iodide. Stir well with a glass rod to release oxygen, add a few drops of phenolphthalein indicator and agitate at moderate speed with a mechanical stirrer. While stirring, titrate slowly with 0.1N HCl to complete disappearance of the pink color.

8.5.2 Calculate the titratable hydroxide alkali as follows:

$$\text{Ca}(\text{OH})_2 \text{ g/L} = \frac{V \times A \times 37.00}{10}$$

where:

$V$  = volume of HCl, mL

$A$  = normality of HCl

8.6 Chlorate, if present in the bleach liquor, is not included in any of the previously described available chlorine or total chlorine determinations.

8.7 This method was reclassified as a Classical Method by committee action in 1997.

## 9. Related methods

CPPA J.2 "Analysis of Calcium Hypochlorite Bleaching Powder, Bleach Liquor, and Bleach Sludge" (historical method) and APPITA P 600 "Analysis of Bleaching Powder, Bleach Liquor, and Bleach Sludge" (withdrawn).

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