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T \_\_\_\_\_ 266 \_\_\_\_\_

BALLOT NO. \_\_\_\_\_ 02 - SARG \_\_\_\_\_

DRAFT NO. \_\_\_\_\_ 02 \_\_\_\_\_

DATE \_\_\_\_\_ May 16, 2024 \_\_\_\_\_

WORKING GROUP  
CHAIR \_\_\_\_\_ Dennis Crawshaw \_\_\_\_\_

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 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.

## **Determination of Sodium, Calcium, Copper, Iron and Manganese in Pulp and Paper by Atomic Absorption Spectroscopy**

*(Five-year review of Official Method T 266 om-18)*

*(Changes from Draft 1 shown through strikethroughs/underlines)*

### **1. Scope**

1.1 This method describes the determination of sodium, calcium, copper, iron, and manganese in pulp, paper, and wood by atomic absorption spectroscopy.

1.2 This method may also be applicable to other elements, provided that they do not volatilize in the process. [For example, zinc and cadmium can be determined by atomic absorption spectroscopy.](#)

1.3 For alternate procedures see these methods which have been reclassified as Classical Methods: TAPPI T 241 "Manganese in Pulp," TAPPI T 242 "Iron in Pulp," TAPPI T 243 "Copper in Pulp," TAPPI T 247 "Calcium in Pulp," and TAPPI T 623 "Sodium Determination by the Uranyl Zinc Acetate Method." A modern alternative method used by many analytical laboratories is inductively coupled plasma atomic emission spectroscopy (ICP-AES).

## 2. Summary

The specimen is ashed, and the ash is dissolved in hydrochloric acid. The elements are determined with an atomic absorption spectrophotometer against calibrated standards.

## 3. Significance

3.1 Sodium content of pulp can reflect on washing during the process. Sodium content of paper may be caused by a contamination, e.g., sea water, or be an additive, e.g., salt to improve conductivity.

3.2 Calcium in dissolving pulps can cause difficulties in viscose spinning and film casting operations.

3.3 Copper may interfere with the color of dyes to be used in the pulp, has an adverse effect on paper permanence, and affects dissolving pulp quality.

3.4 Iron in pulp can cause discoloration and problems in photographic and blueprint papers, has an adverse effect on paper permanence, and affects dissolving pulp quality.

3.5 Manganese in pulp acts as a catalyst in oxidizing cellulose; i.e., it adversely affects paper permanence and affects dissolving pulp quality.

## 4. Apparatus

4.1 Atomic absorption spectrophotometer and appropriate hollow cathode lamps.<sup>1</sup>

4.2 Muffle furnace.

4.3 Crucibles, platinum, zirconium or quartz.

**NOTE 1:** The crucible must be cleaned carefully; spots are to be removed by rubbing with fine sand. Boil the crucible four times in 6M HCl.

4.4 *Miscellaneous:* volumetric flasks, pipets. All glassware should be acid washed, carefully rinsed with ultrapure water, and dried prior to use.

## 5. Reagents

5.1 *Hydrochloric acid, 6M.* Add carefully 500 mL of concentrated HCl (sp gr 1.19) to approximately 450 mL deionized water. Make to a total volume of 1 L with deionized water.

**NOTE 2:** Water used for atomic absorption work must be free of metal ions. Ordinary distilled water shall be passed through a deionizing system prior to usage. Water with the purity of ASTM Type II reagent water is recommended (1).

5.2 Standard solutions of sodium, calcium, copper, iron, and manganese.

**NOTE 3:** It is possible to purchase ultrapure standard solutions for metals, rather than preparing standards from pure reagents or metals. Purchased standards can be used but with one **CAUTION:** Single element standards are generally certified only for the single element of choice and therefore may contain other elemental contamination. Do not, therefore, attempt to make multielement standards in one flask.

5.2.1 *Sodium solution, 1000 mg/L.* Dissolve 2.542 g of sodium chloride, NaCl, in 1 L of deionized water.

5.2.2 *Calcium solution, 1000 mg/L.* Add 50 mL of deionized water to 2.498 g of primary standard calcium carbonate, CaCO<sub>3</sub>. Add dropwise a minimum volume of HCL (approximately 20 mL) to effect complete dissolution of the CaCO<sub>3</sub>. Dilute to 1 L with deionized water.

5.2.3 *Copper solution, 1000 mg/L.* Dissolve 1.000 g of copper metal in a minimum volume of (1 + 1) HNO<sub>3</sub>. Dilute to 1 L with 1% (v/v) HNO<sub>3</sub>.

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<sup>1</sup>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 Quality and Standards Department.

5.2.4 *Iron solution*, 1000 mg/L. Dissolve 1.000 g of iron wire in 50 mL of (1 + 1) HNO<sub>3</sub>. Dilute to 1 L with deionized water.

5.2.5 *Manganese solution*, 1000 mg/L. Dissolve 2.749 g of manganese (manganous) sulfate (MnSO<sub>4</sub>) dried at 300°C in 1 L of deionized water.

5.3 *Lanthanum chloride*. Wet 59 g of lanthanum oxide (La<sub>2</sub>O<sub>3</sub>) with 50 mL of water. Slowly add 250 mL of concentrated HCl to dissolve the La<sub>2</sub>O<sub>3</sub>. Dilute to 1 L with deionized water. Use 10 mL of this solution per 50 mL volume of every calibration standard or test solution when calcium is to be determined. (**CAUTION:** Use extreme care in this preparation due to safety concerns, adding water to acid.)

**NOTE 4:** For the determination of sodium, the effects of ionization will be substantially overcome by the addition of an excess (1000-2000 ppm) of another alkali, e.g., K, or Cs to every calibration and test solution. This should be considered an integral part of the procedure for sodium analysis.

## **6. Procedure**

6.1 Determine the moisture content of the sample according to TAPPI T 550 "Determination of Equilibrium Moisture in Pulp, Paper, and Paperboard for Chemical Analysis."

6.2 Weigh a 10-g specimen to the nearest 0.01 g in a tared, clean crucible in duplicate. Ash the specimen in a furnace at 525° ± 25°C until the carbon has been totally burned away. The sample should not be allowed to flame.

**NOTE 5:** By mutual consent wet ashing may be used.

6.3 Remove and cool the crucible taking extreme care to avoid any losses. Add cautiously 5 mL of 6M HCl and evaporate to near dryness, not allowing any portion of the bottom of the beaker to go dry. Add another 5 mL of 6M HCl and evaporate to near dryness. Finally, add 5 mL of 6M HCl and heat the solution for 5 min. Filter out the insoluble silicates, if any are present, and transfer the solution quantitatively to a 50-mL volumetric flask with deionized water.

6.4 Make up to the mark.

**NOTE 6:** Rinse all glassware with 6M HCl and deionized water.

6.5 Set up the spectrophotometer according to the manufacturer's recommendation as to lamp current, burner, flame, slit, etc. Recommended lines to the nearest nm are 423 (calcium), 325 (copper), 248 (iron), 279 (manganese), and 589 (sodium). The iron 248.3 line is preferred over the 248.8 line.

6.6 Prepare calibration solutions by diluting the standard solution to the concentrations shown in volumetric flasks. To make sure the standard solutions matrix is equal to the blank add 6M HCl to each (e.g., 5 mL 6M HCl in 50 mL).

Sodium:	0.2, 0.4, 0.6 and, 0.8 mg/L (add 1000-2000 ppm K or Cs)
Manganese:	0.2, 0.4, 1, and 2 mg/L
Iron:	1, 2, 3, and 4 mg/L
Copper:	0.2, 0.5, 0.7, and 1 mg/L
Calcium:	0.5, 1, 2.5, and 5 mg/L (add lanthanum chloride reagent)
Blank:	5 mL 6M HCl in 50 mL

**NOTE 7:** The calibration solutions must be made to the same acid concentration as the test solutions.

**NOTE 8:** Instruments with a curve correcting microprocessor may need only 2 or 3 calibration standards and work over a wider concentration range.

6.7 Aspirate the calibration solutions in succession until each has reached a steady value on the instrument's readout (null meter, chart trace, or digital readout in either absorbance or concentration). Prepare a calibration graph by plotting the reading against the concentration of the element in mg/L.

6.8 Aspirate each specimen solution twice as in 6.7, and record the result. It is recommended that *at least one calibration solution and the blank* be aspirated as a check after every five samples.

6.9 Dilute the specimen solution using blank matrix solution if the first reading is beyond the calibration curve. This could be necessary, particularly for calcium.

6.10 Determine the concentration of the element in the solution using the calibration graph if not so given by the direct readout of concentration.

## 7. Calculation and report

7.1 Use the following equations to calculate results.

Element concentration in mg/kg (ppm) =

$$\frac{(\text{mg/L in test solution}) \times 50 \times d}{\text{sample wt., g (dry wt. basis)}}$$

$$d = \frac{\text{volume of diluted test solution, mL}}{\text{Aliquot of test solution used, mL}}$$

Where no further dilution is done after section 6.4,  $d = 1$ .

Sample wt., g (dry wt. basis) =

$$\frac{(100 - \% \text{ moisture in sample}) \times \text{sample wt., g}}{100}$$

7.2 Report average of two determinations and note any large variations.

## 8. Precision

Based on limited (and sometimes conflicting) data (1-4), the best estimates of precision available at this time are shown in Table 1. Repeatability and reproducibility are used as defined in TAPPI T 1200 "Interlaboratory Evaluation of Test Methods to Determine TAPPI Repeatability and Reproducibility" each of which is the average of two test determinations.

Table 1. Precision.

Element	Test range, ppm	Repeatability	Reproducibility
Sodium	19	20%	...
	380	5%	...
Calcium	85-2400	14%	35%
	13-15	14%	170%
Copper	0.5-13	33%	112%
Iron	3-93	2.1 ppm	9.5 ppm
Manganese	0.2-0.3	10%	460%
	0.6-40	21%	81%
	80	1.7%	...

**NOTE 9:** Precision is given in percent of test values (percent of parts per million) except for iron, where precision is given in the same units as the test values (that is, in parts per million). This 1983 repeatability data is similar to data developed by ISO in 1996. Precision estimates for ISO are %CV from 6% to 11% for calcium (ISO 777-2001), %CV from 23% to 73% for copper (ISO 778 – 2001), and % CV from 4% to 45% for iron (ISO 777 – 2001). All %CV data is for bleached pulp, coated paperboard, uncoated paperboard, and copy paper. All data includes four samples and eight laboratories by SCAN using AA or plasma emission spectroscopy. There are no ISO comparisons for sodium or manganese.

## 9. Keywords

Pulp, Paper, Sodium, Calcium, Copper, Iron, Manganese, Atomic absorption spectroscopy, Spectroscopy

## 10. Additional Information

- 10.1 Effective date of issue: To Be Assigned.
- 10.2 This method is a replacement for TAPPI T 241, TAPPI T 242, TAPPI T 243, TAPPI T 247, and TAPPI T 623, each of which has been reclassified as a Classical Method.
- 10.3 Test specimen size is fairly large to reduce the effect of nonhomogeneity of the sample.
- 10.4 Related methods: ISO 777, 778, 779, 1930.
- 10.5 In this 2011 edition, a note was added to provide more details on the precision data.

## References

ASTM D 1193 “Standard Specification for Reagent Water,” American Society for Testing and Materials, West Conshohocken, PA.

### Literature cited

1. Jones, J. B., and Isaac, R. A., “Comparative Elemental Analyses of Plant Tissue by Spark Emission and Atomic Absorption Spectroscopy,” *Agronomy J.* **61**(3): 393 (1969); in particular, Table 4.
2. Ant-Wuorinen, O., and Visapää, A., “Determination of the Inorganic Impurities of Cellulose by Atomic Absorption Spectrometry,” *Paperi Puu* **48** (11): 649 (1966); in particular, Table VI.
3. Töppel, O., Griebenow, W., and Wethmann, B., “Die Anwendung der Atom-Absorptions-Spektroskopie auf dem Zellstoff-und Papier-gebiet,” *Das Papier* **31**(12): 509 (1977); in particular, Table 3.
4. “Atomic Absorption Round Robin Data,” ASTM Committee, D-23, September 1974.

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

