

T 610 sp-11

TENTATIVE STANDARD – 1932
OFFICIAL STANDARD – 1933
REVISED – 1975
OFFICIAL TEST METHOD – 1982
REVISED – 1987
REVISED – 1992
STANDARD PRACTICE – 1997
REVISED – 2002
REAFFIRMED - 2006
REAFFIRMED - 2011
©2011 TAPPI

The information and data contained in this document were prepared by a technical committee of the Association. The committee and the Association assume no liability or responsibility in connection with the use of such information or data, including but not limited to any liability under patent, copyright, or trade secret laws. The user is responsible for determining that this document is the most recent edition published.

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.

Preparation of indicators and standard solutions

1. Scope

This method describes preparation of frequently used indicator solutions and preparation and standardization of frequently used volumetric reagent solutions (usually called “standard solutions”) required in TAPPI Test Methods.

2. Significance

Precision of the test methods for volumetric analysis depends to a large extent upon the procedures of preparation and standardization of reagent solutions. Describing and combining the recommended procedures for commonly used indicators and standard solutions in one method eliminates the necessity for covering such details in all of the test methods wherein the solutions are used.

3. Apparatus

- 3.1 *Balance*, analytical, single-pan or two-pan, readability of 0.1 mg.

NOTE 1: Testing procedures for evaluating the performance of balances are described in ANSI/ASTM Standard E319 (1).

- 3.2 *Balance weights* (for two-pan balances), Class 1 or 2, meeting ANSI/ASTM specifications (2).

3.3 *Volumetric glassware*: volumetric flasks, burets, and pipets, Class A, meeting ANSI/ASTM specifications (3, 4, 5). Calibration of the volumetric glassware is described in ANSI/ASTM Standard E542 (6) and in most textbooks of inorganic analysis. Calibrated and certified glassware are also available commercially.

Approved by the Standard Specific Interest Group for this Standard Practice



Documents

Document Sharing Hub

4. Reagents

4.1 *Reagent grade chemicals*, for preparation of indicators and standard solutions. The chemicals must meet the A.C.S. specifications (7).

4.2 *Primary standard grade chemicals*, for standardization of the solutions. Primary standard grade chemicals are available from the National Bureau of Standards (8) or from chemical suppliers.

4.3 *Ethanol* (ethyl alcohol), $\text{CH}_3\text{CH}_2\text{OH}$, 95%, conforming with A.C.S. specifications (7).

4.4 *Carbon dioxide-free water*. In a 1000-mL Erlenmeyer flask, boil 700 - 800 mL of water for 30 min. Stopper the flask with a rubber stopper fitted to a drying tube containing a CO_2 -absorbent material. Cool to room temperature and use soon after preparation. Larger volumes of carbon dioxide-free water can be prepared by bubbling nitrogen gas through the water for 1 to 2 h, using a fritted glass gas dispersion tube.

4.5 Distilled or deionized water used in this entire test method must conform with A.C.S. specifications (7) or with ANSI/ASTM D1193 (9), Type I or II.

5. Indicators

5.1 Introduction

5.1.1 Most of the chemicals for preparation of indicator solutions are available in two forms: as sodium salts soluble in water and free acid form soluble in ethanol. Both forms of the indicators can be used, although sodium salts are recommended for convenience.

5.1.2 Indicator solutions are prepared normally in 0.1% concentration, e.g., 0.1 g of an indicator dissolved in 100 mL of water or ethanol.

5.1.3 The visual transition intervals listed here are in accordance with the A.C.S. specifications (7). Slightly different pH values for some indicators could be found in other publications.

5.1.4 More distinct color changes can be obtained in some cases by using mixed indicators as described in particular TAPPI Test Methods.

NOTE 2: Prepared indicator solutions are also available commercially.

5.2 *Methyl orange*; pH 3.2 (pink or red) - pH 4.4 (yellow): Dissolve the methyl orange sodium salt in water.

5.3 *Methyl red*; pH 4.2 (pink) - pH 6.2 (yellow): Dissolve the methyl red hydrochloride in ethanol, or methyl red sodium salt in water.

5.4 *Phenol red*; pH 6.8 (yellow) - pH 8.2 (red): Dissolve the phenol red in ethanol, or phenol red sodium salt in water. Add 0.1N NaOH solution dropwise until the color changes to orange.

5.5 *Phenolphthalein*; pH 8.0 (colorless) - pH 10.0 (red): Dissolve phenolphthalein in 95% ethanol. Neutralize if necessary by adding 0.1N NaOH solution dropwise until a faint pink color appears, then just remove the color with a drop or two of 0.1N HCl.

5.6 *Bromophenol blue*; pH 3.0 (yellow) - pH 4.6 (blue): Dissolve the bromophenol blue in ethanol, or bromophenol blue sodium salt in water.

5.7 *Thymol blue*; pH 8.0 (yellow) - pH 9.2 (blue): Dissolve the thymol blue in ethanol, or thymol blue sodium salt in water.

5.8 *Potassium chromate indicator*: Dissolve 25 g of potassium chromate, K_2CrO_4 , in about 200 mL water. Add a few drops of 2.5% AgNO_3 solution, sufficient to precipitate any chloride (black-red precipitate). Filter and dilute to 250 mL with water.

5.9 *"Ferrous" indicator*: Dissolve 1.5 g of 1.10-phenanthroline monohydrate, $\text{C}_{12}\text{H}_8\text{N}_2 \cdot \text{H}_2\text{O}$, and 0.7 g of ferrous sulfate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, in 100 mL water.

5.10 *Starch indicator*: So-called "soluble starch" and "iodometric indicators" are available under various trade names. They can be dissolved in water (2 - 3 g/L) or added in dry form near the endpoint to the solutions being titrated. These indicators must meet the A.C.S. specifications for soluble starch (7).

6. Standard solutions

6.1 Introduction

6.1.1 In general, preparation of 0.1N solutions is described in this method. Solutions of other normalities, as specified in TAPPI Test Methods, are prepared by using proportionally more or less of the reagents. Standard solutions of less than 0.1N could also be prepared by dilution of a stronger solution, followed by restandardization.

NOTE 3: Most of the commonly used standard solutions are also available commercially. The strength of the solutions may be changed on storage, and the exact normality of the solutions should be verified before use.

6.1.2 It is recommended to prepare the standard solutions slightly over-strength at first. Then add the required volume of water and restandardize.

6.1.3 The solutions shall be standardized and diluted to the final volume at a temperature of $20 \pm 0.5^\circ\text{C}$. If the solutions are not made up at 20°C , the volume could be corrected according to Table 1 (see Additional Information 9.5).

Table 1. Temperature corrections*

Value, mL	Correction to be added, mL					Correction to be subtracted, mL									
	15°	16°	17°	18°	19°	21°	22°	23°	24°	25°	26°	27°	28°	29°	30°
5	0.004	0.003	0.002	0.002	0.001	0.001	0.002	0.003	0.004	0.005	0.006	0.007	0.009	0.010	0.011
10	0.008	0.006	0.005	0.003	0.002	0.002	0.004	0.006	0.008	0.010	0.012	0.015	0.018	0.020	0.023
15	0.011	0.009	0.007	0.005	0.003	0.003	0.006	0.009	0.012	0.015	0.019	0.022	0.028	0.030	0.034
20	0.015	0.013	0.010	0.007	0.004	0.004	0.008	0.012	0.016	0.020	0.025	0.030	0.035	0.040	0.046
25	0.018	0.016	0.012	0.008	0.004	0.004	0.009	0.014	0.020	0.025	0.031	0.037	0.044	0.050	0.057
30	0.023	0.020	0.015	0.010	0.005	0.005	0.011	0.017	0.024	0.029	0.037	0.045	0.053	0.061	0.069
35	0.027	0.022	0.017	0.012	0.006	0.006	0.013	0.020	0.028	0.034	0.044	0.052	0.062	0.071	0.080
40	0.030	0.025	0.020	0.014	0.007	0.007	0.015	0.023	0.032	0.039	0.050	0.060	0.070	0.081	0.092
45	0.034	0.028	0.022	0.015	0.008	0.008	0.017	0.026	0.036	0.046	0.056	0.067	0.079	0.091	0.103
50	0.038	0.031	0.024	0.017	0.009	0.009	0.019	0.029	0.040	0.051	0.063	0.075	0.088	0.101	0.115
100	0.076	0.063	0.049	0.034	0.018	0.018	0.038	0.058	0.080	0.102	0.126	0.150	0.176	0.202	0.229

*In using burets all corrections may be rounded off to the nearest 0.01 mL, whereas the next decimal place should be used in accurate work with pipets smaller than 25 mL. For normal solutions the above corrections should be increased by 50% and for 0.5N solutions by 25%.

6.1.4 Standard solutions shall be stored in cool and dark places. Iodine, permanganate, and silver nitrate solutions must be kept in dark-colored bottles. Normality of the standard solutions shall be verified at intervals not exceeding one month. Frequent restandardization is required for some standard solutions (6.6; 6.8; 6.10).

6.2 Hydrochloric acid and sulfuric acid

6.2.1 *Preparation.* The following table shows the approximate amount of concentrated acids needed to make 1000 mL of a standard solution:

Normality of a solution	Concentrated HCl approx. 12N	Concentrated H ₂ SO ₄ density 1.84 g/mL, approx. 36N
0.01	0.83 mL	0.30 mL or 0.55 g
0.05	4.15 mL	1.50 mL or 2.76 g
0.1	8.3 mL	3.00 mL or 5.52 g
0.5	41.5 mL	15.0 mL or 27.6 g
1.0	83.0 mL	30.0 mL or 55.2 g

6.2.2 *Standardization.* Place a few grams of primary standard grade sodium carbonate (about 99.95% Na₂CO₃) in a weighing bottle and heat in an oven at $250 \pm 5^\circ\text{C}$ for 4 h (Note 4). Cool in a desiccator and weigh rapidly, to the nearest 0.1 mg, an amount sufficient to give a titration of about 40 mL. For standardization of 0.1N acid, use 0.21 g of sodium carbonate, for 0.5N acid use 1.05 g, etc. [See section 9.3 for alternate standardization procedure using tris (hydroxymethyl) aminomethane.]

NOTE 4: Ordinary reagent grade sodium carbonate contains 99.5 - 99.7% Na₂CO₃ and shall be purified by washing with ethanol before use. Pure sodium carbonate could also be prepared by heating reagent grade sodium bicarbonate, NaHCO₃, in a shallow dish at $275 \pm 5^\circ\text{C}$ with frequent stirring for 2 h. (If not heated to completion, however, this can lead to erroneous results.)

Dissolve the carbonate in 50 mL water, add 3 drops of methyl red indicator, and titrate with the acid to the point where the color changes to red. Boil the solution carefully, to avoid loss, until the color is discharged. Cool to room