



Designation: D686 – 93 (Reapproved 2007)

An American National Standard

Standard Test Methods of Qualitative Examination of Mineral Filler and Mineral Coating of Paper¹

This standard is issued under the fixed designation D686; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 These test methods cover two procedures for the qualitative determination and identification of the mineral constituents of filled and coated papers.

1.2 Due to the similarity in chemical composition and physical size and shape of some of the various possible constituents contained in a given paper specimen, more precise, quantitative methods may at times be required for positive identification.

1.3 It is recommended that one become thoroughly familiar with these test methods by analyzing paper samples of known mineral component content.

1.4 The test methods appear as follows:

Method A—Qualitative Chemical Analysis	Sections 4 to 11
Method B—Microscopical Identification	12 to 19

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

NOTE 1—These test methods are technically equivalent to TAPPI T 421.

2. Referenced Documents

2.1 ASTM Standards:²

D585 Practice for Sampling and Accepting a Single Lot of Paper, Paperboard, Fiberboard, and Related Product

D586 Test Method for Ash in Pulp, Paper, and Paper Products³

¹ These test methods are under the jurisdiction of ASTM Committee D06 on Paper and Paper Products and are the direct responsibility of Subcommittee D06.92 on Standard Documents Relating to Paper and Paper Products.

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

³ Withdrawn.

D921 Discontinued 1980; Method of Test for Titanium Dioxide in Paper³

D1030 Test Method for Fiber Analysis of Paper and Paperboard

2.2 TAPPI Standards:⁴

T 401 Fiber analysis of paper and paperboard

T 438 Zinc and cadmium in paper and pigments

T 421 Qualitative (Including Optical Microscopic) Analysis of Mineral Filler and Mineral Coating of Paper

3. Significance and Use

3.1 Qualitative chemical analyses of the mineral component of a paper specimen, Test Method A, serve to identify the ions of any such minerals. The results may then be interpreted in terms of the minerals themselves. Direct identification of some of these minerals or their ions is frequently possible using optical microscopical examination, Test Method B. For additional information, see Annex A1.

3.2 The analysis can be considerably simplified if it is desired only to establish the presence or absence of a particular filler.

3.3 A microscopical examination of the ash usually proves to be a useful adjunct to chemical analysis, and if possible should be attempted (see Sections 12-18).

Test Method A—Qualitative Chemical Analysis

4. Apparatus

4.1 *Crucible*, platinum, with lid, for use in 9.7.1 and in ashing the sample that is being examined. Porcelain or silica crucibles may be used if their weight does not change under the ignition conditions.

4.2 *Muffle Furnace*, electric, controlled to maintain a temperature of $525 \pm 25^\circ\text{C}$.

4.3 *Laboratory Oven*, electric, controlled to maintain a temperature of $150 \pm 3^\circ\text{C}$.

4.4 *Blowpipe*.

4.5 *Wire Loop*, platinum.

⁴ Available from Technical Association of the Pulp and Paper Industry (TAPPI), 15 Technology Parkway South, Norcross, GA 30092, http://www.tappi.org.

4.6 *Spot Plate*, black, glazed.

4.7 *Other Apparatus*—Beakers, 250-mL; watch glass; volumetric flasks, 100-mL; filter funnels and fairly rapid, low-ash filter paper,⁵ and Bunsen burner.

5. Reagents

5.1 *Acetic Acid*, (*Glacial*, 99.7 % $\text{CH}_3\text{-COOH}$, *sp gr* 1.05), approximately 1 *N* solution. Add approximately 11.5 mL glacial acetic acid to 50 mL water in a volumetric flask and dilute to 100-mL mark.

5.2 *Ammonium Chloride Solution* (NH_4OH , 10 %).

5.3 *Ammonium Hydroxide* (*sp gr* 0.90)—Concentrated ammonium hydroxide (NH_4OH).

5.4 *Ammonium Oxalate Solution* ($(\text{NH}_4)_2\text{-C}_2\text{O}_4\text{H}_2\text{O}$, 3.5 %).

5.5 *Ammonium Sulfate*, $(\text{NH}_4)_2\text{SO}_4$.

5.6 *Barium Chloride Solution* (BaCl_2 , 10 %).

5.7 *Charcoal Black*.

5.8 *Cobalt Nitrate Solution*—Dissolve 8 g of cobalt nitrate ($\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$) in 100 mL of water.

5.9 *Diphenylthiocarbazone (Dithizone) Solution*—Dissolve 10 mg dithizone in 100 mL carbon tetrachloride, (CCl_4).

5.10 *Hydrochloric Acid* (2 *N*, *sp gr* 1.19)—Concentrated hydrochloric acid (HCl). Add 15 mL of concentrated HCl to approximately 75 mL water in a 100-mL volumetric flask, cool, and dilute to 100-mL mark.

5.11 *Hydrogen Peroxide* (30 % H_2O_2), or a solution of 3 % H_2O_2 used in proportionately greater quantities. Extreme caution should be used when handling 30 % H_2O_2 solution as it is very active when in contact with skin. Eye protection should be worn.

5.12 *Iodine Solution* (0.1 *N*).

5.13 *Lead Acetate Paper*—Immerse strips of filter paper in a saturated solution of lead acetate ($\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$); withdraw from solution and allow to air dry.

5.14 *Lime Water*, saturated solution. Dissolve about 0.2 g of calcium hydroxide ($\text{Ca}(\text{OH})_2$) in 100 mL of water and filter.

5.15 *Magnesium Reagent*—Dissolve 0.5 g of par-nitrobenzeneazoresorcinol in 100 mL of sodium hydroxide (NaOH) solution (1 %).

5.16 *Microcosmic Salt Solution*—Dissolve 5 g of sodium ammonium phosphate ($\text{NaNH}_4\text{HPO}_4 \cdot 4\text{H}_2\text{O}$) in water and dilute to 100 mL.

5.17 *Morin* (3,5,7,2',4'-pentahydroxyflavanone)—Saturated solution of morin in methyl alcohol.

5.18 *Potassium Dichromate Solution* ($\text{K}_2\text{Cr}_2\text{O}_7$, 4 %).

5.19 *Potassium Ferrocyanide Solution*—Dissolve 15 g of ($\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$) in 1000 mL of water.

5.20 *Potassium Hydroxide Solution* (2 *N*)—Dissolve 11.2 g of potassium hydroxide (KOH) in 75 mL water; cool and dilute to 100 mL.

5.21 *Sodium Carbonate*—Powdered sodium carbonate (Na_2CO_3).

5.22 *Sodium Hydroxide Solution* (2 *N*). Dissolve 8 g (NaOH) in 75 mL water; cool and dilute to 100 mL.

⁵ Whatman No. 40, available from A. H. Thomas Co., P. O. Box 779, Philadelphia, PA 19105, or its equivalent, has been found satisfactory for these test methods.

5.23 *Sulfuric Acid* (5 %, *sp gr* 1.84)—Concentrated sulfuric acid (H_2SO_4). Add 3 mL of concentrated H_2SO_4 to 75 mL of water, cool, dilute to 100 mL.

6. Purity of Reagents

6.1 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.⁶ 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.

7. Sampling

7.1 Obtain a sample of the paper to be tested in accordance with Practice D585.

8. Test Specimens

8.1 From each test unit, for each complete determination, cut test specimens of sufficient size to yield at least 0.15 g of ash.

8.2 An additional specimen of each test unit should be available for testing without previous ashing.

9. Procedure

9.1 An outline scheme of the qualitative procedure is given in Fig. 1.

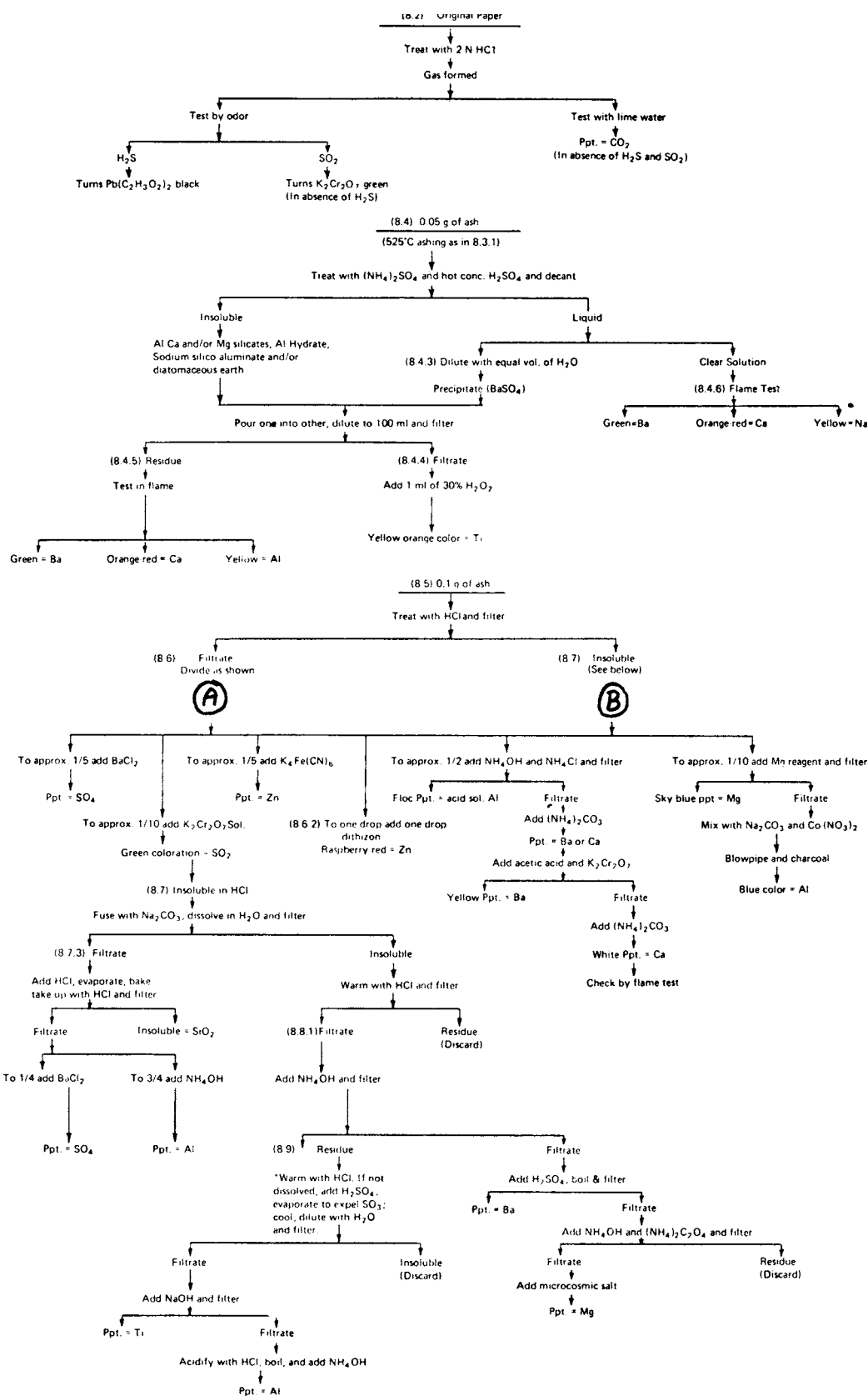
9.2 *Sulfite, Sulfide, and Carbonate (Unignited Coating or Paper Sample)*:

9.2.1 Treat a portion of the unignited coating or paper sample in a small beaker or test tube with 2 *N* HCl . Note whether effervescence takes place and the odor of any escaping gas. Liberation of SO_2 and H_2S indicates the presence of sulfites and sulfides, respectively. Warm the contents of the beaker and test the vapor with moistened lead acetate paper. The development of a metallic gray or black color confirms the presence of sulfide. In the absence of sulfides, add either a small crystal of potassium dichromate or a few drops of a 4 % dichromate solution to a small portion of the HCl solution of the sample. A green coloration indicates the presence of a reducing agent, in this case probably a sulfite.

NOTE 2—Mixtures of sulfites and sulfides are not known to be used in loading or coating paper.

9.2.2 If sulfites and sulfides are absent, effervescence alone is a good indication of the presence of a carbonate, which may be confirmed by holding a glass rod with a drop of saturated lime water just above the solution. Cloudiness (milky) appearance of the supported drop indicates the presence of CO_2 . This precipitate may later dissolve. A confirmatory test of CO_2 in the presence of sulfites is to oxidize the sulfites to sulfates by

⁶ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For Suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.



*This procedure is necessary only if both Ti and HCl insoluble Al compounds are present and it is necessary to estimate relative amounts of Ti and Al.

FIG. 1 Qualitative Analysis of Mineral Filler and Mineral Coating of Paper

adding to the contents of the beaker, a weak solution of iodine (about 0.1 *N*), drop by drop, until the entire liquid is colored yellow. Then test with lime water on a glass rod as described previously in this paragraph.

9.3 Ashing:

9.3.1 Ash the specimen at a temperature of 525°C (lower than the 925°C temperature used in Test Method **D586** (see also **9.3.2**)). This lower temperature is used to prevent or minimize the alteration of the composition of various coating or filling components.

9.3.2 For coated paper where separate analyses of filling material and coating minerals are desired, remove the coating by an enzymatic stripping procedure. Evaporate to dryness the aqueous mixture containing the coating minerals and ash this residue as well as the base stock in accordance with **9.3.1**.

NOTE 3—If synthetic coating adhesives have been used in place of starch or casein, enzymatic stripping will not be effective. In this case, scrape the coating from the surface with a razor blade.

9.4 Aluminum Hydrate: Sodium Silicoaluminate; Aluminium (Al), Calcium (Ca), or Magnesium (Mg) Silicates; Ca or Barium (Ba) Sulfates; Titanium Dioxide (TiO₂):

9.4.1 To approximately 0.05 g of ash add 10 g of (NH₄)₂SO₄ and 20 mL of concentrated H₂SO₄. Cover with a watch glass and boil vigorously for at least 3 min.

9.4.2 Considerable undissolved matter indicates the presence of one or more of the following: sodium silicoaluminate; Ca, Al, or Mg silicate; aluminum hydrate or diatomaceous earth. If this strongly acidic, hot solution is clear, the absence of these materials is confirmed. Calcium or barium sulfate, or both, will be dissolved unless the specimen being tested weighs more than 0.05 g; TiO₂ will be in the solution.

9.4.3 Decant some of the supernatant liquid into a small beaker, cool, and cautiously dilute it with a portion (up to about five times its volume) of cold water. The formation of a precipitate on dilution indicates the presence of barium sulfate, which is relatively soluble in hot concentrated H₂SO₄.

9.4.4 Mix the diluted acidic mixture (**9.4.3**) with the remainder of the undiluted strongly acidic mixture (**9.4.2**) from the concentrated H₂SO₄ treatment and add sufficient water to make the ratio of H₂O to H₂SO₄ about 5:1. If the original H₂SO₄ solution (**9.4.1**) was clear, dilute it 5:1 by adding water cautiously after cooling. Filter and retain any residue for examination under **9.4.5**. To the cooled filtrate add 1 mL of 30 % H₂O₂. A deep yellow or orange color indicates the presence of titanium, the depth of color being proportional to the amount of titanium present. If only a very light yellow color is produced, it may be caused by titanium from clay, or derived from dissolved titanium in the mill water.

9.4.5 The presence of barium or calcium in any insoluble residue (**9.4.4**) can be determined by a flame test as follows: Dip a clean platinum wire into the moist residue, retained on the filter paper, and hold it in a Bunsen flame. A green flame indicates the presence of barium, a red flame indicates calcium, and a yellow to colorless flame indicates aluminum or magnesium silicates, or both, or aluminum hydrate.

NOTE 4—Calcium sulfate (CaSO₄) is quite soluble in diluted H₂SO₄ and may not be observed at this step.

9.4.6 The flame test can be used to detect soluble calcium, barium, and sodium in the clear solution obtained in **9.4.3**. Cautiously dilute a small portion of the solution with an equal volume of water. Dip a clean platinum wire into the solution and hold it in a Bunsen flame. A green flame indicates barium, a red flame indicates calcium, and a strong yellow flame indicates sodium.

9.5 Sulfide, Sulfite, and Carbonate (Ash Sample Ignited at 525°C):

9.5.1 Treat 0.1 g of ash (**9.3.1**) with 10 mL of water and 5 mL of concentrated HCl in a small-sized beaker. Effervescence, as in **9.2.1**, indicates the presence of a carbonate or sulfite. Withdraw 1 or 2 mL of the solution and add two drops of 4 % K₂Cr₂O₇ solution. A green coloration indicates sulfite.

9.5.2 Heat the contents of the beaker to boiling and test the fumes with moistened lead acetate paper; the development of a metallic gray or black color indicates the presence of sulfides. These tests should be checked by tests made on the original specimen of paper since carbonates may be lost. Sulfates may be reduced to sulfites or sulfides, or sulfites and sulfides oxidized to sulfates, depending on the temperature and oxidizing conditions during ignition.

NOTE 5—If the temperature of ashing is around 925°C as specified in Test Method **D586**, no carbonates are present and any sulfites probably would have been oxidized to sulfates.

9.5.3 Boil the mixture for at least 5 min unless complete solution occurs sooner. Add 35 mL of water, and again heat to boiling. If this solution is not clear, filter through a fairly rapid, low-ash filter paper and wash twice with water, reserving the filtrate for analysis of the acid-soluble portion. Wash the insoluble residue thoroughly and discard the washings. Reserve the acid-insoluble portion retained on the filter paper for later treatments in accordance with **9.7**.

9.6 Sulfate, Zinc (Zn), Mg, Al, Ba, Ca:

9.6.1 To approximately one fifth of the acid-soluble portion from **9.5.3** add 1 mL of CaCl₂ solution. A precipitate that appears immediately or after heating for 10 min shows the presence of sulfates. To another one-fifth portion add a few millilitres of potassium ferrocyanide solution. A heavy white precipitate indicates the presence of zinc. The presence of zinc may be confirmed by the red color produced in the following dithizone test.

9.6.2 Place one drop of the acid-soluble portion from **9.5.3** on a watch glass and add one drop of 2 *N* NaOH and a few drops of dithizone solution. The carbon tetrachloride (CCl₄) is evaporated by gentle blowing while stirring with a glass rod. A raspberry-red solution confirms the presence of zinc. The color of any precipitate can be disregarded.

9.6.3 To a small portion of the remaining three fifths of the filtered solution (**9.5.3**) (about one tenth of the total) add one or two drops of the magnesium reagent and render alkaline with NaOH solution; a sky blue precipitate indicates the presence of magnesium. However, other minerals commonly used in paper give a violet (distinguished from sky-blue) coloration to the solution. Take care not to add an excess of the reagent, because it may mask the blue precipitate if magnesium is present. If in doubt, filter the solution and examine the filter paper for the presence of a blue precipitate.