

This document is not an ASTM standard and is intended only to provide the user of an ASTM standard an indication of what changes have been made to the previous version. Because it may not be technically possible to adequately depict all changes accurately, ASTM recommends that users consult prior editions as appropriate. In all cases only the current version of the standard as published by ASTM is to be considered the official document.



■ Designation: **E 165 – 9502**

An American National Standard

## Standard Test Method for Liquid Penetrant Examination<sup>1</sup>

This standard is issued under the fixed designation E 165; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

---

■ <sup>1</sup> This test method is under the jurisdiction of ASTM Committee ~~E-7~~ E07 on Nondestructive Testing and is the direct responsibility of Subcommittee E07.03 on Liquid Penetrant and Magnetic Particle Methods.

■ Current edition approved ~~Jan. 15, 1995~~; February 10, 2002. Published ~~March 1995~~; April 2002. Originally published as E 165 – 60 T. Last previous edition E 165 – 945.

## 1. Scope

1.1 This test method<sup>2</sup> covers procedures for penetrant examination of materials. They are nondestructive testing methods for detecting discontinuities that are open to the surface such as cracks, seams, laps, cold shuts, laminations, through leaks, or lack of fusion and are applicable to in-process, final, and maintenance examination. They can be effectively used in the examination of nonporous, metallic materials, both ferrous and nonferrous, and of nonmetallic materials such as glazed or fully densified ceramics, certain nonporous plastics, and glass.

1.2 This test method also provides a reference:

1.2.1 By which a liquid penetrant examination process recommended or required by individual organizations can be reviewed to ascertain its applicability and completeness.

1.2.2 For use in the preparation of process specifications dealing with the liquid penetrant examination of materials and parts. Agreement by the user and the supplier regarding specific techniques is strongly recommended.

1.2.3 For use in the organization of the facilities and personnel concerned with the liquid penetrant examination.

1.3 This test method does not indicate or suggest criteria for evaluation of the indications obtained. It should be pointed out, however, that after indications have been produced, they must be interpreted or classified and then evaluated. For this purpose there must be a separate code or specification or a specific agreement to define the type, size, location, and direction of indications considered acceptable, and those considered unacceptable.

1.4 The values stated in inch-pound units are to be regarded as the standard. SI units are provided for information only.

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.* For specific hazard statements, see Note 5, Note 12, and Note 20.

## 2. Referenced Documents

### 2.1 ASTM Standards:

D 129 Test Method for Sulfur in Petroleum Products (General Bomb Method)<sup>3</sup>

D 516 Test Method for Sulfate Ion in Water<sup>4</sup>

D 808 Test Method for Chlorine in New and Used Petroleum Products (Bomb Method)<sup>3</sup>

D 1193 Specification for Reagent Water<sup>4</sup>

D 1552 Test Method for Sulfur in Petroleum Products (High-Temperature Method)<sup>3</sup>

D 4327 Test Method for Anions in Water by Chemically Suppressed Ion Chromatography<sup>4</sup>

E 433 Reference Photographs for Liquid Penetrant Inspection<sup>5</sup>

E 543 Practice for Evaluating Agencies that Perform Nondestructive Testing<sup>5</sup>

E 1208 Test Method for Fluorescent Liquid Penetrant Examination Using the Lipophilic Post-Emulsification Process<sup>5</sup>

E 1209 Test Method for Fluorescent Liquid Penetrant Examination Using the Water-Washable Process<sup>5</sup>

E 1210 Test Method for Fluorescent Liquid Penetrant Examination Using the Hydrophilic Post-Emulsification Process<sup>5</sup>

E 1219 Test Method for Fluorescent Liquid Penetrant Examination Using the Solvent-Removable Process<sup>5</sup>

E 1220 Test Method for Visible Penetrant Examination Using the Solvent-Removable Process<sup>5</sup>

E 1316 Terminology for Nondestructive Examinations<sup>5</sup>

E 1418 Test Method for Visible Penetrant Examination Using the Water-Washable Process<sup>5</sup>

### 2.2 ASNT Document:<sup>6</sup>

Recommended Practice SNT-TC-1A for Nondestructive Testing Personnel Qualification and Certification

ANSI/ASNT CP-189 Standard for Qualification and Certification of Nondestructive Testing Personnel

### 2.3 Military Standard:

MIL-STD-410 Nondestructive Testing Personnel Qualification and Certification<sup>7</sup>

### 2.4 APHA Standard:

429 Method for the Examination of Water and Wastewater<sup>8</sup>

### 2.5 AIA Standard:

NAS-410 Certification and Qualification of Nondestructive Test Personnel<sup>6</sup>

## 3. Terminology

3.1 The definitions relating to liquid penetrant examination, which appear in Terminology E 1316, shall apply to the terms used in this standard.

<sup>2</sup> For ASME Boiler and Pressure Vessel Code applications see related Recommended Test Method SE-165 in the Code.

<sup>3</sup> Annual Book of ASTM Standards, Vol 05.01.

<sup>4</sup> Annual Book of ASTM Standards, Vol 11.01.

<sup>5</sup> Annual Book of ASTM Standards, Vol 03.03.

<sup>6</sup> Available from the American Society for Nondestructive Testing, 1711 Arlingate Lane, Columbus, OH 43228-0518.

<sup>7</sup> Available from Standardization Documents Order Desk, Bldg. 4 Section D, 700 Robbins Ave., Philadelphia, PA 19111-5094, Attn: NPODS.

<sup>8</sup> Available from American Public Health Association, Publication Office, 1015 Fifteenth Street, NW, Washington, DC 20005.

#### 4. Summary of Test Method

4.1 A liquid penetrant which may be a visible or a fluorescent material is applied evenly over the surface being examined and allowed to enter open discontinuities. After a suitable dwell time, the excess surface penetrant is removed. A developer is applied to draw the entrapped penetrant out of the discontinuity and stain the developer. The test surface is then examined to determine the presence or absence of indications.

NOTE 1—The developer may be omitted by agreement between purchaser and supplier.

NOTE 2—**Caution:** Fluorescent penetrant examination shall not follow a visible penetrant examination unless the procedure has been qualified in accordance with 10.2, because visible dyes may cause deterioration or quenching of fluorescent dyes.

4.2 Processing parameters, such as surface precleaning, penetration time and excess penetrant removal methods, are determined by the specific materials used, the nature of the part under examination, (that is, size, shape, surface condition, alloy) and type of discontinuities expected.

#### 5. Significance and Use

5.1 Liquid penetrant examination methods indicate the presence, location and, to a limited extent, the nature and magnitude of the detected discontinuities. Each of the various methods has been designed for specific uses such as critical service items, volume of parts, portability or localized areas of examination. The method selected will depend accordingly on the service requirements.

#### 6. Classification of Penetrations and Methods

6.1 Liquid penetrant examination methods and types are classified as shown in Table 1.

6.2 *Fluorescent penetrant examination* utilizes penetrants that fluoresce brilliantly when excited by black light (see 8.9.1.2). The sensitivity of fluorescent penetrants depends on their ability to be retained in the various size discontinuities during processing, then to bleed out into the developer coating and produce indications that will fluoresce. Fluorescent indications are many times brighter than their surroundings when viewed under black light illumination.

6.3 *Visible penetrant examination* uses a penetrant that can be seen in visible light. The penetrant is usually red, so that the indications produce a definite contrast with the white background of the developer. The visible penetrant process does not require the use of black light. However, visible penetrant indications must be viewed under adequate white light (see 8.9.2.1).

#### 7. Types of Materials

7.1 *Liquid penetrant examination materials* (see Notes ~~3-5~~ **3 and 4**) consist of fluorescent and visible penetrants, emulsifiers (oil-base and ~~water-base; fast and slow acting~~), water-base, solvent removers and developers. A family of liquid penetrant examination materials consists of the applicable penetrant and emulsifier or remover, as recommended by the manufacturer. Intermixing of ~~materials~~ penetrants and emulsifiers from various manufacturers is not recommended.

NOTE 3—Refer to 9.1 for special requirements for sulfur, halogen and alkali metal content.

NOTE 4—**Caution:** While approved penetrant materials will not adversely affect common metallic materials, some plastics or rubbers may be swollen or stained by certain penetrants. ~~Note 5—Warning: These materials may be flammable or emit hazardous and toxic vapors. Observe all manufacturer's instructions and precautionary statements.~~

##### 7.2 Penetrants:

7.2.1 *Post-Emulsifiable Penetrants* are designed to be insoluble in water and cannot be removed with water rinsing alone. They are designed to be selectively removed from the surface using a separate emulsifier. The emulsifier, properly applied and given a proper emulsification time, combines with the excess surface penetrant to form a water-washable mixture, which can be rinsed from the surface, leaving the surface free of fluorescent background. Proper emulsification time must be experimentally established and maintained to ensure that over-emulsification does not occur, resulting in loss of indications.

7.2.2 *Water-Washable Penetrants* are designed to be directly water-washable from the surface of the test part, after a suitable penetrant dwell time. Because the emulsifier is “built-in” to the water-washable penetrant, it is extremely important to exercise proper process control in removal of excess surface penetrant to ensure against overwashing. Water-washable penetrants can be washed out of discontinuities if the rinsing step is too long or too vigorous. Some penetrants are less resistant to overwashing than others.

**TABLE 1 Classification of Penetrant Examination Types and Methods**

Type I—Fluorescent Penetrant Examination
Method A—Water-washable (see Test Method E 1209)
Method B—Post-emulsifiable, lipophilic (see Test Method E 1208)
Method C—Solvent removable (see Test Method E 1219)
Method D—Post-emulsifiable, hydrophilic (see Test Method E 1210)
Type II—Visible Penetrant Examination
Method A—Water-washable (see Test Method E 1418)
Method C—Solvent removable (see Test Method E 1220)

7.2.3 *Solvent-Removable Penetrants* are designed so that excess surface penetrant can be removed by wiping until most of the penetrant has been removed. The remaining traces should be removed with the solvent remover (see 8.6.4.1). To minimize removal of penetrant from discontinuities, care should be taken to avoid the use of excess solvent. Flushing the surface with solvent to remove the excess penetrant is prohibited.

### 7.3 Emulsifiers:

7.3.1 *Lipophilic Emulsifiers* are oil-miscible liquids used to emulsify the excess oily penetrant on the surface of the part, rendering it water-washable. The rate of diffusion establishes the emulsification time. They are either slow- or fast-acting, depending on their viscosity and chemical composition, and also the surface roughness of the area being examined (see 8.6.2).

7.3.2 *Hydrophilic Emulsifiers* are water-miscible liquids used to emulsify the excess oily fluorescent penetrant on the surface of the part, rendering it water-washable (see 8.6.3). These water-base emulsifiers (detergent-type removers) are supplied as concentrates to be diluted with water and used as a dip or spray. The concentration, use and maintenance shall be in accordance with manufacturer's recommendations.

7.3.2.1 Hydrophilic emulsifiers function by displacing the excess penetrant film from the surface of the part through detergent action. The force of the water spray or air/mechanical agitation in an open dip tank provides the scrubbing action while the detergent displaces the film of penetrant from the part surface. The emulsification time will vary, depending on its concentration, which can be monitored by the use of a suitable refractometer.

7.4 *Solvent Removers* function by dissolving the penetrant, making it possible to wipe the surface clean and free of excess penetrant as described in 8.6.1.2 and 8.6.4.

7.5 *Developers*—Development of penetrant indications is the process of bringing the penetrant out of open discontinuities through blotting action of the applied developer, thus increasing the visibility of the indications.

7.5.1 *Dry Powder Developers* are used as supplied (that is, free-flowing, non-caking powder) in accordance with 8.8.2. Care should be taken not to contaminate the developer with fluorescent penetrant, as the penetrant specks can appear as indications.

7.5.2 *Aqueous Developers* are normally supplied as dry powder particles to be either suspended or dissolved (soluble) in water. The concentration, use and maintenance shall be in accordance with manufacturer's recommendations (see 8.8.3).

~~NOTE 6—~~ **5—Caution:** Aqueous developers may cause stripping of indications if not properly applied and controlled. The procedure should be qualified in accordance with 10.2.

7.5.3 *Nonaqueous Wet Developers* are supplied as suspensions of developer particles in a nonaqueous solvent carrier ready for use as supplied. Nonaqueous, wet developers form a coating on the surface of the part when dried, which serves as the developing medium (see 8.8.4).

~~NOTE 7—~~ **6—Caution:** This type of developer is intended for application by spray only.

7.5.4 *Liquid Film Developers* are solutions or colloidal suspensions of resins/polymer in a suitable carrier. These developers will form a transparent or translucent coating on the surface of the part. Certain types of film developer may be stripped from the part and retained for record purposes (see 8.8.5).

## 8. Procedure

8.1 The following ~~general~~ processing guidelines apply to both fluorescent and visible penetrant examination methods (see Figs. 1-3) to both fluorescent and visible penetrant examination methods (see Fig. 4)-3).

8.2 *Temperature Limits*—The temperature of the penetrant materials and the surface of the part to be processed should be between ~~50~~ 40° and ~~100~~ 100°F (~~10~~ 125°F (4° and ~~38~~ 52°C)). Where it is not practical to comply with these temperature limitations, qualify the procedure as described in 10.2 at the temperature of intended use and as agreed to by the contracting parties.

8.3 *Surface Conditioning Prior to Penetrant Examination* —Satisfactory results usually may be obtained on surfaces in the as-welded, as-rolled, as-cast, or as-forged conditions (or for ceramics in the densified conditions). Sensitive penetrants are generally less easily rinsed away and are therefore less suitable for rough surfaces. When only loose surface residuals are present, these may be removed by wiping with clean lint-free cloths. However, precleaning of metals to remove processing residuals such as oil, graphite, scale, insulating materials, coatings, and so forth, should be done using cleaning solvents, vapor degreasing or chemical removing processes. Surface conditioning by grinding, machining, polishing or etching shall follow shot, sand, grit or vapor blasting to remove the peened skin and when penetrant entrapment in surface irregularities might mask the indications of unacceptable discontinuities or otherwise interfere with the effectiveness of the examination. For metals, unless otherwise specified, etching shall be performed when evidence exists that previous cleaning, surface treatments or service usage have produced a surface condition that degrades the effectiveness of penetrant examination. (See A1.1.1.8 for precautions.)

~~NOTE 87—~~ When agreed between purchaser and supplier, grit blasting without subsequent etching may be an acceptable cleaning method.

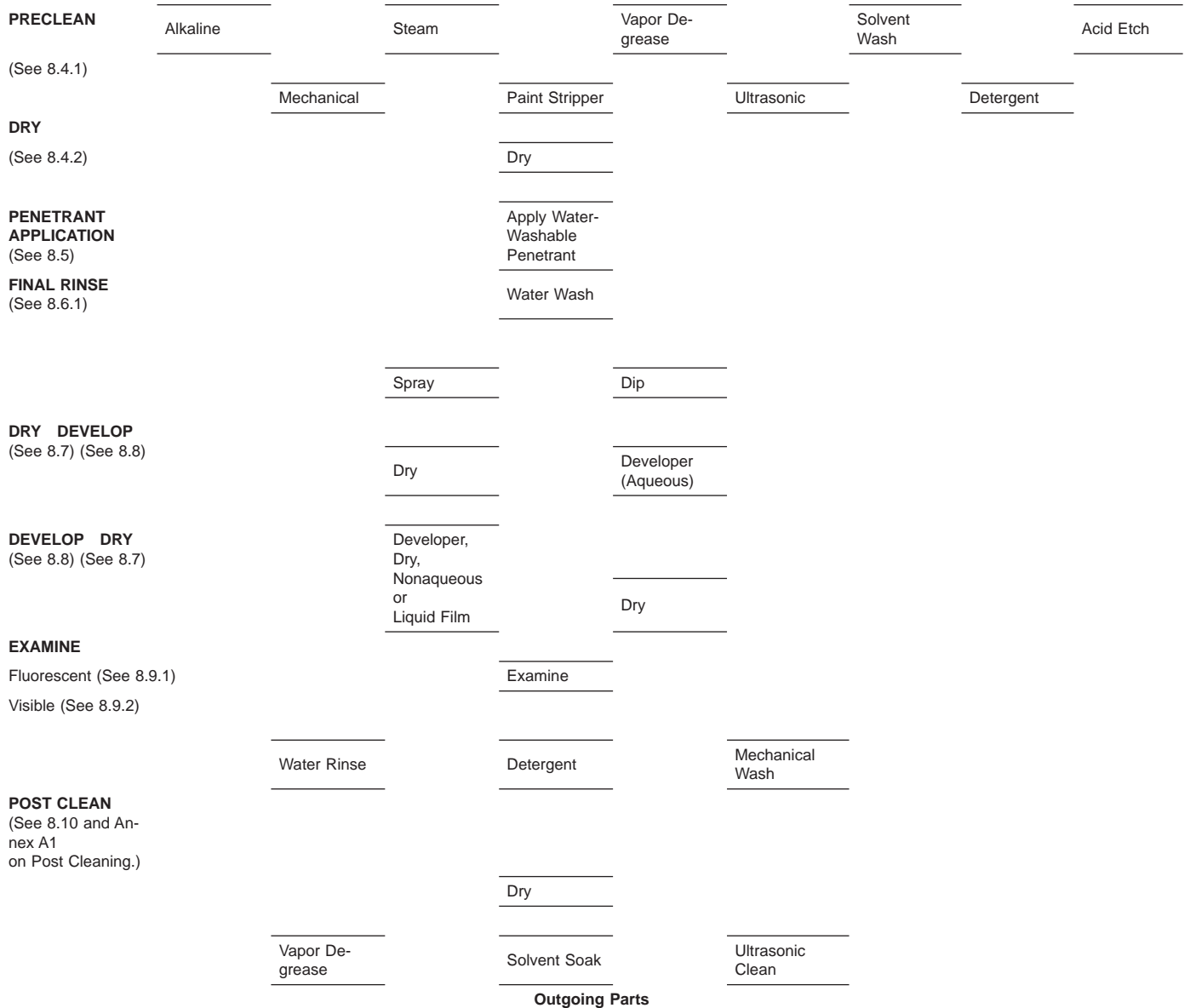
~~NOTE 9—~~ **8—Caution:** Sand or shot blasting may possibly close discontinuities and extreme care should be used with grinding and machining operations to avoid masking discontinuities.

~~NOTE 10—~~ ~~For~~ **9—For** structural or electronic ceramics, surface preparation by grinding, sand blasting and etching for penetrant examination is not recommended because of the potential for damage.

### 8.4 Removal of Surface Contaminants :

8.4.1 *Precleaning*—The success of any penetrant examination procedure is greatly dependent upon the surrounding surface and discontinuity being free of any contaminant (solid or liquid) that might interfere with the penetrant process. All parts or areas of

Incoming Parts



**FIG. 1 General Procedure Flowsheet for Penetrant Examination Using the Water-Washable Process (Test Method E 1209 for Fluorescent and Test Method E 1220 for Visible Light)**

parts to be examined must be clean and dry before the penetrant is applied. If only a section of a part, such as a weld, including the heat affected zone is to be examined, all contaminants shall be removed from the area being examined as defined by the contracting parties. “Clean” is intended to mean that the surface must be free of rust, scale, welding flux, weld spatter, grease, paint, oily films, dirt, and so forth, that might interfere with the penetrant process. All of these contaminants can prevent the penetrant from entering discontinuities (see Annex on Cleaning of Parts and Materials).

**NOTE 1H—Caution:** Residues from cleaning processes such as strong alkalis, pickling solutions and chromates, in particular, may adversely react with the penetrant and reduce its sensitivity and performance.

**8.4.2 Drying after Cleaning—**It is essential that the surface of parts be thoroughly dry after cleaning, since any liquid residue will hinder the entrance of the penetrant. Drying may be accomplished by warming the parts in drying ovens, with infrared lamps, forced hot air, or exposure to ambient temperature.

**8.5 Penetrant Application—**After the part has been cleaned, dried, and is within the specified temperature range, the penetrant is applied to the surface to be examined so that the entire part or area under examination is completely covered with penetrant.

**8.5.1 Modes of Application—**There are various modes of effective application of penetrant such as dipping, brushing, flooding, or spraying. Small parts are quite often placed in suitable baskets and dipped into a tank of penetrant. On larger parts, and those

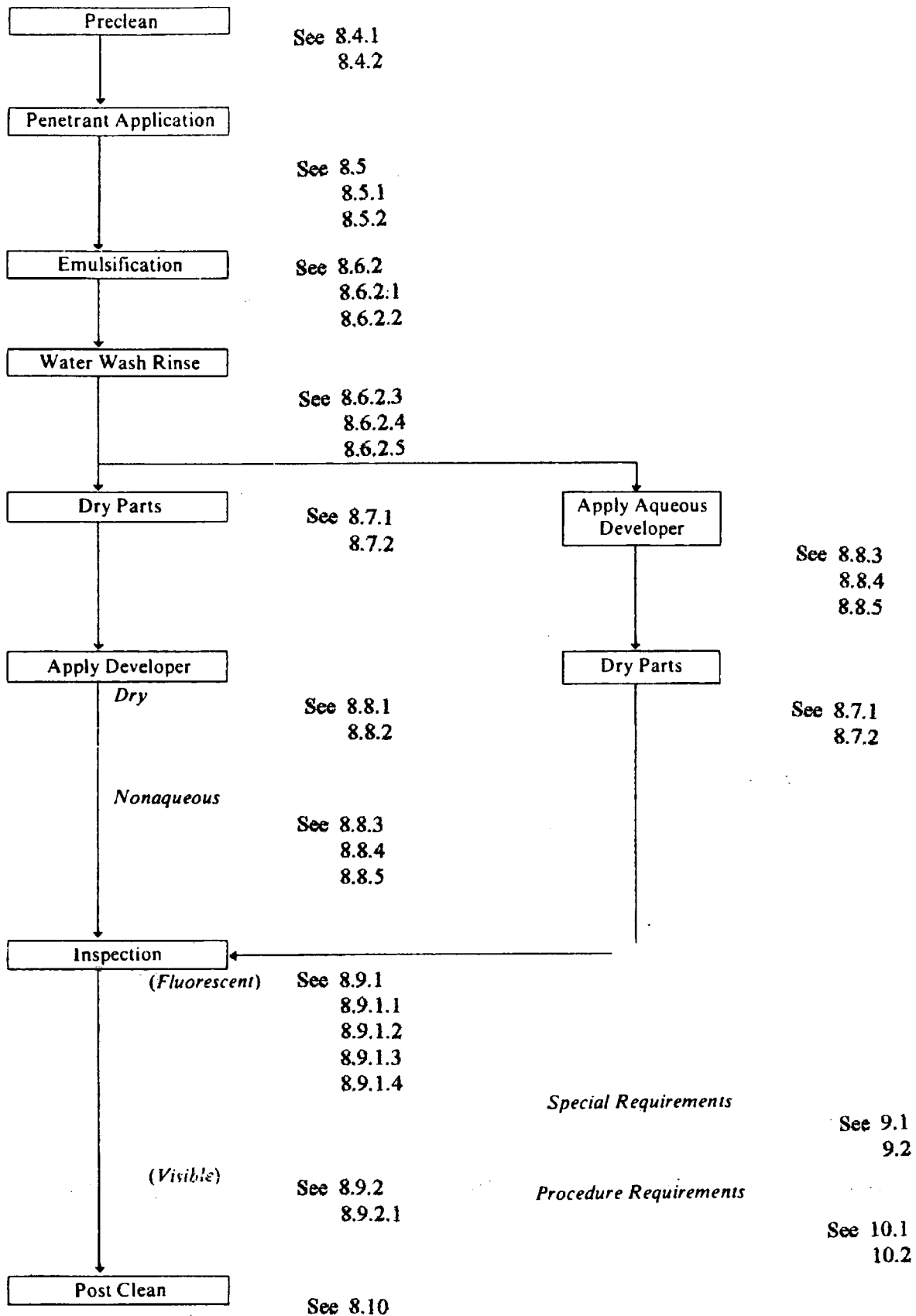
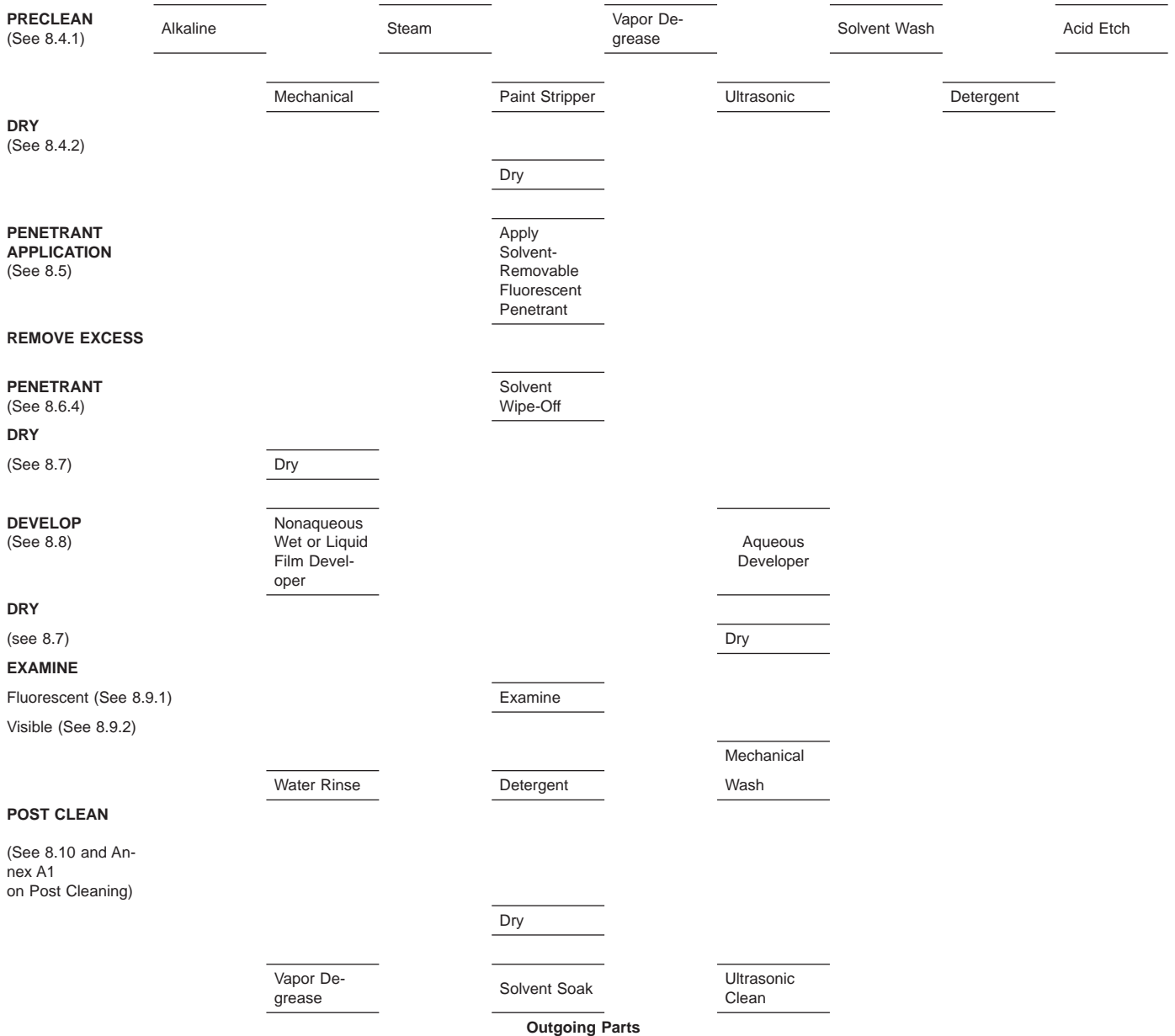


FIG. 2 General Procedure Flowsheet for Post-emulsifiable Method

Incoming Parts



Outgoing Parts

**FIG. 3 Solvent-Removable Penetrant Examination General Procedure Flowsheet (Test Method E 1219 for Fluorescent and Test Method E 1220 for Visible Light)**

with complex geometries, penetrant can be applied effectively by brushing or spraying. Both conventional and electrostatic spray guns are effective means of applying liquid penetrants to the part surfaces. Electrostatic spray application can eliminate excess liquid build-up of penetrant on the part, minimize overspray, and minimize the amount of penetrant entering hollow-cored passages which might serve as penetrant reservoirs, causing severe bleedout problems during examination. Aerosol sprays are conveniently portable and suitable for local application.

NOTE 121—**Caution:** Not all penetrant materials are suitable for electrostatic spray applications, so tests should be conducted prior to use.

NOTE 132—**Warning:** With spray applications, it is important that there be proper ventilation. This is generally accomplished through the use of a properly designed spray booth and exhaust system.

8.5.2 *Penetrant Dwell Time*—After application, allow excess penetrant to drain from the part (care should be taken to prevent pools of penetrant from forming on the part), while allowing for proper penetrant dwell time (see Table 2). The length of time the penetrant must remain on the part to allow proper penetration should be as recommended by the penetrant manufacturer. Table 2, however, provides a guide for selection of penetrant dwell times for a variety of materials, forms, and types of discontinuity. Unless otherwise specified, the dwell time shall not exceed the maximum recommended by the manufacturer.

**TABLE 2 Recommended Minimum Dwell Times**

Material	Form	Type of Discontinuity	Dwell Times <sup>A</sup> (minutes)	
			Penetrant <sup>B</sup>	Developer <sup>C</sup>
Aluminum, magnesium, steel, brass and bronze, titanium and high-temperature alloys	castings and welds	cold shuts, porosity, lack of fusion, cracks (all forms)	5	10
	wrought materials—extrusions, forgings, plate	laps, cracks (all forms)	10	10
Carbide-tipped tools		lack of fusion, porosity, cracks	5	10
Plastic	all forms	cracks	5	10
Glass	all forms	cracks	5	10
Ceramic	all forms	cracks, porosity	5	10

<sup>A</sup> For temperature range from 50 to 100°F (10 to 38°C) for fluorescent penetrants and 50 to 125°F (10 to 52°C) for visible penetrant.

<sup>B</sup> Maximum penetrant dwell time in accordance with 8.5.2.

<sup>C</sup> Development time begins as soon as wet developer coating has dried on surface of parts (recommended minimum). Maximum development time in accordance with 8.8.6.

NOTE 143—For some specific applications in structural ceramics (for example, detecting parting lines in slip-cast material), the required penetrant dwell time should be determined experimentally and may be longer than that shown in Table 1 and its notes.

### 8.6 Penetrant Removal

#### 8.6.1 Water Washable:

8.6.1.1 *Removal of Excess Penetrant*—After the required penetration time, the excess penetrant on the surface being examined must be removed with water, usually a washing operation. It can be washed off manually, by the use of automatic or semi-automatic water-spray equipment or by immersion. For immersion rinsing, parts are completely immersed in the water bath with air or mechanical agitation. Accumulation of water in pockets or recesses of the surface must be avoided. If the final rinse step is not effective, as evidenced by excessive residual surface penetrant after rinsing, dry (see 8.7) and reclean the part, then reapply the penetrant for the prescribed dwell time.

(a) ~~The~~ The temperature of the water should be relatively constant and should be maintained within the range of 50° to 100°F (10° to 38°C).

(b) ~~Spray-rinse~~ water pressure should not be greater than 40 psi (280 kPa).

(c) ~~Rinse~~ Rinse time should not exceed 120 s unless otherwise specified by part of material specification.

NOTE 154—**Caution:** Avoid overwashing. Excessive washing can cause penetrant to be washed out of discontinuities. With fluorescent penetrant methods perform the rinsing operation under black light so that it can be determined when the surface penetrant has been adequately removed.

8.6.1.2 *Removal by Wiping*—In special applications, penetrant removal may be performed by wiping the surface with a clean, absorbent material dampened with water until the excess surface penetrant is removed, as determined by examination under black light for fluorescent methods and white light for visible methods.

#### 8.6.2 Lipophilic Emulsification:

8.6.2.1 *Application of Emulsifier*—After the required penetration time, the excess penetrant on the part must be emulsified by immersing or flooding the parts with the required emulsifier (the emulsifier combines with the excess surface penetrant and makes the mixture removable with water rinsing). After application of the emulsifier, the parts are drained in a manner that prevents the emulsifier from pooling on the part(s).

8.6.2.2 *Emulsification Dwell Time* begins as soon as the emulsifier has been applied. The length of time that the emulsifier is allowed to remain on a part and in contact with the penetrant is dependent on the type of emulsifier employed and the surface condition (smooth or rough). Nominal emulsification time should be as recommended by the manufacturer. The actual emulsification time must be determined experimentally for each specific application. The surface finish (roughness) of the part is a significant factor in the selection of and in the emulsification time of an emulsifier. Contact time should be kept to the least possible time consistent with an acceptable background and should not exceed the maximum time specified for the part or material.

8.6.2.3 *Post Rinsing*—Effective post rinsing of the emulsified penetrant from the surface can be accomplished using either manual, semi-automated, or automated water immersion or spray equipment or combinations thereof.

8.6.2.4 *Immersion*—For immersion post rinsing, parts are completely immersed in the water bath with air or mechanical agitation. The time and temperature should be kept constant.

(a) ~~The~~ The maximum dip-rinse time should not exceed 120 s unless otherwise specified by part or material specification.  
 (b) ~~The~~ The temperature of the water should be relatively constant and should be maintained within the range of 50° to 100°F (10° to 38°C). **Caution:** A touch-up rinse may be necessary after immersion.

8.6.2.5 *Spray Post Rinsing*—Effective post rinsing following emulsification can also be accomplished by either manual or automatic water spray rinsing of the parts as follows:

(a) ~~Control~~ Control rinse water temperature within the range of 50° to 100°F (10° to 38°C).

(b) ~~Spray~~ Spray rinse water pressure should be in accordance with manufacturers' recommendations. not exceed 40 psi (275 kPa).

(c) ~~The~~ The maximum spray rinse time should not exceed 120 s unless otherwise specified by part or materials specification.



8.6.2.6 *Rinse Effectiveness*—If the emulsification and final rinse step is not effective, as evidenced by excessive residual surface penetrant after emulsification and rinsing, dry (see 8.7) and reclean the part and reapply the penetrant for the prescribed dwell time.

### 8.6.3 *Hydrophilic Emulsification* :

8.6.3.1 *Prerinsing*—Directly after the required penetration time, it is recommended that the parts be prerinsed with water prior to emulsification (8.6.3.3). This step allows for the removal of excess surface penetrant from the parts prior to emulsification so as to minimize the degree of penetrant contamination in the hydrophilic emulsifier bath, thereby extending its life. In addition, prerinsing of penetrated parts minimizes possible oily penetrant pollution in the final rinse step of this process. This is accomplished by collecting the prerinsings in a holding tank, separating the penetrant from water.

8.6.3.2 *Prerinsing Controls*—Effective prerinsing is accomplished by either manual or automated water spray rinsing of the parts as follows:

- (a) ~~(a) Water~~ Water should be free of contaminants that could clog spray nozzles or leave a residue on parts.
- (b) ~~(b) Control~~ Control water temperature within the range of 50 to 100°F (10 to 38°C).
- (c) ~~(c) Spray~~ Spray rinse at a water pressure of 25 to 40 psi (175 to 275 kPa).
- (d) ~~(d) Prerinse~~ Prerinse time should be the least possible time (nominally 60 s maximum) to provide a consistent residue of penetrant on parts. Wash time is to be as specified by the part or material specification.
- (e) ~~(e) Remove~~ Remove water trapped in cavities using filtered shop air at a nominal pressure of 25 psi (175 kPa) or a suction device to remove water from pooled areas.

8.6.3.3 *Application of Emulsifier*—After the required penetration time and following the prerinse, the residual surface penetrant on part(s) must be emulsified by immersing the part(s) in a hydrophilic emulsifier bath (8.6.3.4) or by spraying the part(s) with the emulsifier (8.6.3.5) thereby rendering the remaining residual surface penetrant water-washable in the final rinse station (8.6.3.6).

8.6.3.4 *Immersion*—For immersion application, parts are completely immersed in the emulsifier bath. The hydrophilic emulsifier should be gently agitated throughout the contact cycle.

- (a) ~~(a) Bath~~ Bath concentration should be as recommended by the manufacturer. ~~Most hydrophilic emulsifiers are used within the range of 20 to 33 % in water.~~ Nominal use concentration for immersion applications is 20 %.
- (b) ~~(b) Bath~~ Bath temperatures should be maintained between 50 and 100°F (10 to 38°C).
- (c) ~~(c) Immersion contact time should be kept to the minimum time consistent with an acceptable background required for adequate surface removal and should not exceed 120 s or the maximum time stipulated two min. unless otherwise approved by the part or material specification.~~

(d) ~~(d) Emulsifier drain time begins immediately after parts have been withdrawn from the emulsifier tank and continues until the parts are washed in the final rinse station (8.6.3.6). This drain time should be kept to a minimum to avoid over emulsification and should not exceed 90 s. cognizant engineering organization.~~

8.6.3.5 *Spray Application*—For spray application following the prerinse step, parts are emulsified by the spray application of an emulsifier. All part surfaces should be evenly and uniformly sprayed to effectively emulsify the residual penetrant on part surfaces to render it water-washable.

- (a) ~~(a) The~~ The concentration of the emulsifier for spray application should be in accordance with the manufacturer's recommendations, but should not exceed 5 %.
- (b) ~~(b) Temperature~~ Temperature to be maintained at 50 to 100°F (10 to 38°C).
- (c) ~~(c) The~~ The spray pressure should be 25 psi (175 kPa) max for air and 40 psi (280 kPa) max for water.
- (d) ~~(d) Contact~~ Contact time should be kept to the minimum consistent with an acceptable background and should not exceed 120 s or the maximum time stipulated by the part or material specification.

8.6.3.6 *Post-Rinsing of Hydrophilic Emulsified Parts* —Effective post-rinsing of emulsified penetrant from the surface can be accomplished using either manual, semi-automated, or automated water immersion or spray equipment or combinations thereof.

8.6.3.7 *Immersion Post-Rinsing*—Parts are to be completely immersed in the water bath with air or mechanical agitation.

(a) ~~(a) The~~ The temperature of the water should be relatively constant and should be maintained within the range of 50 to 100°F (10 to 38°C).

(b) ~~(b) The~~ The maximum dip rinse time should not exceed 120 s unless otherwise specified by part or material specification.

**Caution:** A touch-up rinse may be necessary after immersion.

8.6.3.8 *Spray Post-Rinsing*—Following emulsification parts can be post-rinsed by water spray rinsing as follows:

- (a) ~~(a) Control~~ Control rinse water temperature within the range of 50 to 100°F (10 to 38°C).
- (b) ~~(b) Spray~~ Spray rinse water pressure should be in accordance with manufacturer's instructions. ~~not exceed 40 psi (275 kPa).~~
- (c) ~~(c) The~~ The maximum spray rinse time should not exceed 120 s unless otherwise specified by part or materials specification.

8.6.3.9 If the emulsification and final rinse steps are not effective, as evidenced by excessive residual surface penetrant after emulsification and rinsing, dry (see 8.7) and reclean the part and reapply the penetrant for the prescribed dwell time.

### 8.6.4 *Solvent-Removable Penetrants* :

8.6.4.1 *Removal of Excess Penetrant*—After the required penetration time, the excess penetrant is removed insofar as possible, by using wipers of a dry, clean, lint-free material and repeating the operation until most traces of penetrant have been removed. Then using a lint-free material lightly moistened with solvent remover the remaining traces are gently wiped to avoid removing

penetrant from discontinuities. Avoid the use of excess solvent. If the wiping step is not effective, as evidenced by difficulty in removing the excess penetrant, dry the part (see 8.7), and reapply the penetrant for the prescribed dwell time. Flushing the surface with solvent following the application of the penetrant and prior to developing is prohibited.

8.7 *Drying*—Drying the surface of the part(s) is necessary prior to applying dry or nonaqueous developers or following the application of the aqueous developer. Drying time will vary with the size, nature, and number of parts under examination.

8.7.1 *Drying Modes—Parts can Parameters—Components shall be air dried by using a hot-air recirculating oven, a hot at room temperature or cold air blast, or by exposure to ambient temperature, particularly when the excess surface penetrant was removed with a solvent. Drying is best done in a thermostatically controlled recirculating hot-air dryer. Local heating or cooling is permitted provided the temperature of the part remains in the range of 50 drying oven. Oven temperatures shall not exceed 160°F (71°C). Drying time shall only be that necessary to 100°F (40 to 38°C) for fluorescent methods and in adequately dry the range of 50 to 125°F (10 to 52°C) for visible methods unless otherwise agreed by part. Components shall be removed from the contracting parties.*

**NOTE 16—Caution:** Drying oven temperature should immediately after drying. Components shall not exceed 160°F (71°C); be placed in the oven with pooled water or pooled aqueous solutions/suspensions.

8.7.2 *Drying Time Limits*—Do not allow parts to remain in the drying oven any longer than is necessary to dry the surface. Times over 30 min in the dryer may impair the sensitivity of the examination.

8.8 *Developer Application:*

8.8.1 *Modes of Application*—There are various modes of effective application of the various types of developers such as dusting, immersing, flooding or spraying. The size, configuration, surface condition, number of parts to be processed, and so forth, will influence the choice of developer application.

8.8.2 *Dry Powder Developer*—Dry powder developers should be applied immediately after drying in such a manner as to ensure complete part coverage. Parts can be immersed in a container of dry developer or in a fluid bed of dry developer. They can also be dusted with the powder developer through a hand powder bulb or a conventional or electrostatic powder gun. It is common and effective to apply dry powder in an enclosed dust chamber, which creates an effective and controlled dust cloud. Other means suited to the size and geometry of the specimen may be used, provided the powder is dusted evenly over the entire surface being examined. Excess powder may be removed by shaking or tapping the part, or by blowing with low-pressure (5 to 10 psi) 5 psi (34 to 70 kPa) dry, clean, compressed air.

**NOTE 175—Caution:** The air stream intensity should be established experimentally for each application.

8.8.3 *Aqueous Developers*—Aqueous soluble developers should not be used with Type 2 penetrants or Type 1, Method A penetrants. Aqueous suspendable developers can be used with both Type 1 and Type 2 penetrants. Aqueous developers should be applied to the part immediately after the excess penetrant has been removed and prior to drying. Aqueous developers should be prepared and maintained in accordance with the manufacturer's instructions and applied in such a manner as to ensure complete, even, part coverage. ~~Caution should be exercised when using an aqueous developer with water-washable penetrants to avoid possible stripping of indications.~~ Aqueous developers may be applied by spraying (see Note 176), flowing, or immersing the part. It is common to immerse the parts in a prepared developer bath. Immerse parts only long enough to coat all of the part surfaces with the developer (see Note 187). Then remove parts from the developer bath and allow to drain. Drain all excess developer from recesses and trapped sections to eliminate pooling of developer, which can obscure discontinuities. Dry the parts in accordance with 8.7. The dried developer coating appears as a translucent or white coating on the part.

**NOTE 186—Caution:** Atomized spraying is not recommended since a spotty film may result.

**NOTE 197—Caution:** If parts are left in the bath too long, indications may leach out.

8.8.4 *Nonaqueous Wet Developers*—After the excess penetrant has been removed and the surface has been dried, apply developer by spraying in such a manner as to ensure complete part coverage with a thin, even film of developer. These types of developer carrier evaporate very rapidly at normal room temperature and do not, therefore, require the use of a ~~dryer (see Note 20) dryer~~. Dipping or flooding parts with nonaqueous developers is prohibited, since they may flush or dissolve the penetrant from within the discontinuities because of the solvent action of these types of developers.

**NOTE 20—18—Warning:** The vapors from the evaporating, volatile solvent developer carrier may be hazardous. Proper ventilation should be provided in all cases, but especially when the surface to be examined is inside a closed volume, such as a process drum or a small storage tank.

8.8.5 *Liquid Film Developers*—Apply by spraying as recommended by the manufacturer. Spray parts in such a manner as to ensure complete part coverage of the area being examined with a thin, even film of developer.

8.8.6 *Developing Time*—The length of time the developer is to remain on the part prior to examination should be not less than 10 min. Developing time begins immediately after the application of dry powder developer and as soon as the wet (aqueous and nonaqueous) developer coating is dry (that is, the solvent carrier has evaporated to dryness). The maximum permitted developing times shall be 4 h for dry powder developer, 2 h for aqueous developers and 1 h for nonaqueous developers.

8.9 *Examination*—Perform examination of parts after the applicable development time as specified in 8.8.6 to allow for bleedout of penetrant from discontinuities into the developer coating. It is good practice to observe the bleedout while applying the developer as an aid in interpreting and evaluating indications.

8.9.1 *Fluorescent Light Examination :*

8.9.1.1 *Visible Ambient Light Level*—Examine fluorescent penetrant indications under black light in a darkened area. Visible ambient light should not exceed 2 ft candles (20 Lx). The measurement should be made with a suitable photographic-type visible light meter on the surface being examined.

8.9.1.2 *Black Light Level Control*—~~Black light intensity, lights shall provide a minimum of 1000  $\mu\text{W}/\text{cm}^2$ , should be measured on at the surface being examined, with a suitable black light meter, examination surface.~~ The black light wavelength shall be in the range of 320 to 380 nm. The intensity should be checked weekly to ensure the required output. Reflectors and filters should be checked daily for cleanliness and integrity. Cracked or broken ultraviolet (UV) filters should be replaced immediately. Defective bulbs, which radiate UV energy, must be replaced before further use. Since a drop in line voltage can cause decreased black light output with consequent inconsistent performance, a constant-voltage transformer should be used when there is evidence of voltage fluctuation.

**Caution:** Certain high-intensity black light may emit unacceptable amounts of visible light, which will cause fluorescent indications to disappear. Care should be taken to use only bulbs certified by the supplier to be suitable for such examination purposes.

NOTE 219—The recommended minimum light intensity in 8.9.1.2 is intended for general usage. For critical examinations, higher intensity levels may be required.

8.9.1.3 *Black Light Warm-Up*—Allow the black light to warm up for a minimum of 10 min prior to its use or measurement of the intensity of the ultraviolet light emitted.

8.9.1.4 *Visual Adaptation*—The examiner should be in the darkened area for at least 1 min before examining parts. Longer times may be necessary under some circumstances.

NOTE 220—**Caution:** Photochromic lenses shall not be worn during examination.

## 8.9.2 *Visible Light Examination:*

8.9.2.1 *Visible Light Level*—Visible penetrant indications can be examined in either natural or artificial light. Adequate illumination is required to ensure no loss in the sensitivity of the examination. A minimum light intensity at the examination site of 100 fc (1000 Lx) is recommended.

8.9.3 *Housekeeping*—Keep the examination area free of interfering debris, including fluorescent objects. Practice good housekeeping at all times.

8.9.4 *Evaluation*—Unless otherwise agreed, it is normal practice to interpret and evaluate the discontinuity based on the size of the indication (see Reference Photographs E 433).

8.10 *Post Cleaning*—Post cleaning is necessary in those cases where residual penetrant or developer could interfere with subsequent processing or with service requirements. It is particularly important where residual penetrant examination materials might combine with other factors in service to produce corrosion. A suitable technique, such as a simple water rinse, waterspray, machine wash, vapor degreasing, solvent soak, or ultrasonic cleaning may be employed (see Annex on Post Cleaning). It is recommended that if developer removal is necessary, it should be carried out as promptly as possible after examination so that it does not “fix” on the part.

NOTE 231—**Caution:** Developers should be removed prior to vapor degreasing. Vapor degreasing can bake the developer on parts.

## 9. Special Requirements

### 9.1 *Impurities:*

9.1.1 When using penetrant materials on austenitic stainless steels, titanium, nickel-base or other high-temperature alloys, the need to restrict impurities such as sulfur, halogens and alkali metals must be considered. These impurities may cause embrittlement or corrosion, particularly at elevated temperatures. Any such evaluation should also include consideration of the form in which the impurities are present. Some penetrant materials contain significant amounts of these impurities in the form of volatile organic solvents. These normally evaporate quickly and usually do not cause problems. Other materials may contain impurities which are not volatile and may react with the part, particularly in the presence of moisture or elevated temperatures.

9.1.2 Because volatile solvents leave the surface quickly without reaction under normal examination procedures, penetrant materials are normally subjected to an evaporation procedure to remove the solvents before the materials are analyzed for impurities. The residue from this procedure is then analyzed in accordance with Test Method D 129, Test Method D 1552, or Test Method D 129 decomposition followed by Test Method D 516, Method B (Turbidimetric Method) for sulfur. The residue may also be analyzed by Test Method D 808 or Annex A2 on Methods for Measuring Total Chlorine Content in Combustible Liquid Penetrant Materials (for halogens other than fluorine) and Annex A3 on Method for Measuring Total Fluorine Content in Combustible Liquid Penetration Materials (for fluorine). An alternative procedure, Annex A4 on Determination of Anions by Ion Chromatography, provides a single instrumental technique for rapid sequential measurement of common anions such as chloride, fluoride, and sulfate. Alkali metals in the residue are determined by flame photometry or atomic absorption spectrophotometry.

NOTE 242—Some current standards indicate that impurity levels of sulfur and halogens exceeding 1 % of any one suspect element may be considered excessive. However, this high a level may be unacceptable for some applications, so the actual maximum acceptable impurity level must be decided between supplier and user on a case by case basis.

9.2 *Evaluated-Temperature Examination*— Where penetrant examination is performed on parts that must be maintained at

elevated temperature during examination, special materials and processing techniques may be required. Such examination requires qualification in accordance with 10.2. Manufacturer's recommendations should be observed.

## 10. Qualification and Requalification

10.1 *Personnel Qualification*—When required by user/supplier agreement, all examination personnel shall be qualified/certified in accordance with a written procedure conforming to the applicable edition of recommended Practice SNT-TC-1A, ANSI/ASNT CP-189, NAS-410, or MIL-STD-410.

10.2 *Procedure Qualification*—Qualification of procedures using times or conditions differing from those specified or for new materials may be performed by any of several methods and should be agreed by the contracting parties. A test piece containing one or more discontinuities of the smallest relevant size is used. The test piece may contain real or simulated discontinuities, providing it displays the characteristics of the discontinuities encountered in product examination.

10.3 *Nondestructive Testing Agency Qualification*—If a nondestructive testing agency as described in Practice E 543 is used to perform the examination, the agency shall meet the requirements of Practice E 543.

10.4 *Requalification* may be required when a change or substitution is made in the type of penetrant materials or in the procedure (see 10.2).

## 11. Keywords

11.1 fluorescent liquid penetrant testing; hydrophilic emulsification; lipophilic emulsification; liquid penetrant testing; nondestructive testing; solvent removable; visible liquid penetrant testing; water-washable methods

## ANNEXES

### (Mandatory Information)

#### A1. CLEANING OF PARTS AND MATERIALS

##### A1.1 Choice of Cleaning Method

A1.1.1 The choice of a suitable cleaning method is based on such factors as: (1) type of contaminant to be removed since no one method removes all contaminants equally well; (2) effect of the cleaning method on the parts; (3) practicality of the cleaning method for the part (for example, a large part cannot be put into a small degreaser or ultrasonic cleaner); and (4) specific cleaning requirements of the purchaser. The following cleaning methods are recommended:

A1.1.1.1 *Detergent Cleaning*—Detergent cleaners are nonflammable water-soluble compounds containing specially selected surfactants for wetting, penetrating, emulsifying, and saponifying various types of soils, such as grease and oily films, cutting and machining fluids, and unpigmented drawing compounds, etc. Detergent cleaners may be alkaline, neutral, or acidic in nature, but must be noncorrosive to the item being inspected. The cleaning properties of detergent solutions facilitate complete removal of soils and contamination from the surface and void areas, thus preparing them to absorb the penetrant. Cleaning time should average 10 to 15 min at 170° to 200°F (77° to 93°C) with moderate agitation, using concentrations (generally 6 to 8 oz/gal or 45 to 60 kg/m<sup>3</sup>) recommended by the manufacturer of the cleaning compound.

A1.1.1.2 *Solvent Cleaning*—There are a variety of solvent cleaners that can be effectively utilized to dissolve such soils as grease and oily films, waxes and sealants, paints, and in general, organic matter. These solvents should be residue-free, especially when used as a hand-wipe solvent or as a dip-tank degreasing solvent. Solvent cleaners are not recommended for the removal of rust and scale, welding flux and spatter, and in general, inorganic soils. **Caution:** Some cleaning solvents are flammable and can be toxic. Observe all manufacturers' instructions and precautionary notes.

A1.1.1.3 *Vapor Degreasing*—Vapor degreasing is a preferred method of removing oil or grease-type soils from the surface of parts and from open discontinuities. It will not remove inorganic-type soils (dirt, corrosion, salts, etc.), and may not remove resinous soils (plastic coatings, varnish, paint, etc.). Because of the short contact time, degreasing may not completely clean out deep discontinuities and a subsequent solvent soak is recommended.

A1.1.1.4 *Alkaline Cleaning:*

(a) ~~(a) Alkaline~~ Alkaline cleaners are nonflammable water solutions containing specially selected detergents for wetting, penetrating, emulsifying, and saponifying various types of soils. Hot alkaline solutions are also used for rust removal and descaling to remove oxide scale which can mask surface discontinuities. Alkaline cleaner compounds must be used in accordance with the manufacturers' recommendations. **Caution:** Parts cleaned by the alkaline cleaning process must be rinsed completely free of cleaner and thoroughly dried by heat prior to the penetrant-inspection examination process (part temperature at the time of penetrant application shall not exceed 125°F (52°C)).

(b) ~~(b) Steam~~ Steam cleaning is a modification of the hot-tank alkaline cleaning method, which can be used for preparation of large, unwieldy parts. It will remove inorganic soils and many organic soils from the surface of parts, but may not reach to the bottom of deep discontinuities, and a subsequent solvent soak is recommended.

A1.1.1.5 *Ultrasonic Cleaning*—This method adds ultrasonic agitation to solvent or detergent cleaning to improve cleaning efficiency and decrease cleaning time. It should be used with water and detergent if the soil to be removed is inorganic (rust, dirt, salts, corrosion products, etc.), and with organic solvent if the soil to be removed is organic (grease and oily films, etc.). After ultrasonic cleaning, parts should be heated to remove the cleaning fluid, then cooled to at least 125°F (52°C), before application of penetrant.

A1.1.1.6 *Paint Removal*—Paint films can be effectively removed by bond release solvent paint remover or disintegrating-type hot-tank alkaline paint strippers. In most cases, the paint film must be completely removed to expose the surface of the metal. Solvent-type paint removers can be of the high-viscosity thickened type for spray or brush application or can be of low viscosity two-layer type for dip-tank application. Both types of solvent paint removers are generally used at ambient temperatures, as received. Hot-tank alkaline strippers are water-soluble powder compounds generally used at 8 to 16 oz/gal (60 to 120 kg/m<sup>3</sup>) of water at 180 to 200°F (82 to 93°C). After paint removal, the parts must be thoroughly rinsed to remove all contamination from the void openings and then thoroughly dried.

A1.1.1.7 *Mechanical Cleaning and Surface Conditioning*—Metal-removing processes such as filing, buffing, scraping, mechanical milling, drilling, reaming, grinding, liquid honing, sanding, lathe cutting, tumble or vibratory deburring, and abrasive blasting, including abrasives such as glass beads, sand, aluminum oxide, ligno-cellulose pellets, metallic shot, etc., are often used to remove such soils as carbon, rust and scale, and foundry adhering sands, as well as to deburr or produce a desired cosmetic effect on the part. *These processes may decrease the effectiveness of the penetrant examination by smearing or peening over metal surfaces and filling discontinuities open to the surface, especially for soft metals such as aluminum, titanium, magnesium, and beryllium alloy.*

A1.1.1.8 *Acid Etching*—Inhibited acid solutions (pickling solutions) are routinely used for descaling part surfaces. Descaling is necessary to remove oxide scale, which can mask surface discontinuities and prevent penetrant from entering. Acid solutions/etchants are also used routinely to remove smeared metal that peens over surface discontinuities. Such etchants should be used in accordance with the manufacturers' recommendations. **Caution:**

NOTE A1.1—Etched parts and materials must be rinsed completely free of etchants, the surface neutralized and thoroughly dried by heat prior to application of penetrants. Acids and chromates can adversely affect the fluorescence of fluorescent materials.

NOTE A1.2—Whenever there is a possibility of hydrogen embrittlement as a result of acid solution/etching, the part should be baked at a suitable temperature for an appropriate time to remove the hydrogen before further processing. After baking, the part shall be cooled to a temperature below 125°F (52°C) before applying penetrants.

A1.1.1.9 *Air Firing of Ceramics*—Heating of a ceramic part in a clean, oxidizing atmosphere is an effective way of removing moisture or light organic soil or both. The maximum temperature that will not cause degradation of the properties of the ceramic should be used.

## A1.2 Post Cleaning

A1.2.1 *Removal of Developer*—Dry powder developer can be effectively removed with an air blow-off (free of oil) or it can be removed with water rinsing. Wet developer coatings can be removed effectively by water rinsing or water rinsing with detergent either by hand or with a mechanical assist (scrub brushing, washing machine, etc.). The soluble developer coatings simply dissolve off of the part with a water rinse.

A1.2.2 Residual penetrant may be removed through solvent action. Vapor degreasing (10 min minimum), solvent soaking (15 min minimum), and ultrasonic solvent cleaning (3 min minimum) techniques are recommended. In some cases, it is desirable to vapor degrease, then follow with a solvent soak. The actual time required in the vapor degreaser and solvent soak will depend on the nature of the part and should be determined experimentally.

## A2. METHODS FOR MEASURING TOTAL CHLORINE CONTENT IN COMBUSTIBLE LIQUID PENETRANT MATERIALS

### A2.1 Scope and Application

A2.1.1 These methods cover the determination of chlorine in combustible liquid penetrant materials, liquid or solid. Its range of applicability is 0.001 to 5 % using either of the alternative titrimetric procedures. The procedures assume that bromine or iodine will not be present. If these elements are present, they will be detected and reported as chlorine. The full amount of these elements will not be reported. Chromate interferes with the procedures, causing low or nonexistent end points. The method is applicable only to materials that are totally combustible.

### A2.2 Summary of Methods

A2.2.1 The sample is oxidized by combustion in a bomb containing oxygen under pressure (**Caution**, see A2.2.1.1). The chlorine compounds thus liberated are absorbed in a sodium carbonate solution and the amount of chloride present is determined titrimetrically either against silver nitrate with the end point detected potentiometrically (Method A) or coulometrically with the end point detected by current flow increase (Method B).

A2.2.1.1 *Safety*—Strict adherence to all of the provisions prescribed hereinafter ensures against explosive rupture of the bomb, or a blow-out, provided the bomb is of proper design and construction and in good mechanical condition. It is desirable, however, that the bomb be enclosed in a shield of steel plate at least ½ in. (12.7 mm) thick, or equivalent protection be provided against unforeseeable contingencies.

### A2.3 Apparatus

A2.3.1 *Bomb*, having a capacity of not less than 300 mL, so constructed that it will not leak during the test, and that quantitative recovery of the liquids from the bomb may be readily achieved. The inner surface of the bomb may be made of stainless steel or any other material that will not be affected by the combustion process or products. Materials used in the bomb assembly, such as the head gasket and leadwire insulation, shall be resistant to heat and chemical action, and shall not undergo any reaction that will affect the chlorine content of the liquid in the bomb.

A2.3.2 *Sample Cup*, platinum, 24 mm in outside diameter at the bottom, 27 mm in outside diameter at the top, 12 mm in height outside and weighing 10 to 11 g, opaque fused silica, wide-form with an outside diameter of 29 mm at the top, a height of 19 mm, and a 5-mL capacity (Note 1), or nickel (Kawin capsule form), top diameter of 28 mm, 15 mm in height, and 5-mL capacity.

NOTE A2.1—Fused silica crucibles are much more economical and longer-lasting than platinum. After each use, they should be scrubbed out with fine, wet emery cloth, heated to dull red heat over a burner, soaked in hot water for 1 h, then dried and stored in a desiccator before reuse.

A2.3.3 *Firing Wire*, platinum, approximately No. 26 B & S gage.

A2.3.4 *Ignition Circuit* (Note A2.2), capable of supplying sufficient current to ignite the nylon thread or cotton wicking without melting the wire.

NOTE A2.2—**Caution:** The switch in the ignition circuit shall be of a type that remains open, except when held in closed position by the operator.

A2.3.5 *Nylon Sewing Thread*, or *Cotton Wicking*, white.

### A2.4 Purity of Reagents

A2.4.1 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.<sup>9</sup> 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.

A2.4.2 Unless otherwise indicated, references to water shall be understood to mean referee grade reagent water conforming to Specification D 1193.

### A2.5 Decomposition

A2.5.1 *Reagents and Materials:*

A2.5.1.1 *Oxygen*, free of combustible material and halogen compounds, available at a pressure of 40 atm (4.05 MPa).

A2.5.1.2 *Sodium Carbonate Solution (50 g Na<sub>2</sub>CO<sub>3</sub>/L)*—Dissolve 50 g of anhydrous Na<sub>2</sub>CO<sub>3</sub> or 58.5 g of Na<sub>2</sub>CO<sub>3</sub>·2O or 135 g of Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O in water and dilute to 1 L.

A2.5.1.3 *White Oil*, refined.

A2.5.2 *Procedure:*

A2.5.2.1 *Preparation of Bomb and Sample*—Cut a piece of firing wire approximately 100 mm in length. Coil the middle section (about 20 mm) and attach the free ends to the terminals. Arrange the coil so that it will be above and to one side of the sample cup. Place 5 mL of Na<sub>2</sub>CO<sub>3</sub> solution in the bomb (Note A2.3), place the cover on the bomb and vigorously shake for 15 s to distribute the solution over the inside of the bomb. Open the bomb, place the sample-filled sample cup in the terminal holder, and insert a short length of thread between the firing wire and the sample. Use of a sample weight containing over 20 mg of chlorine may cause corrosion of the bomb. The sample weight should not exceed 0.4 g if the expected chlorine content is 2.5 % or above. If the sample is solid, not more than 0.2 g should be used. Use 0.8 g of white oil with solid samples. If white oil will be used (Note A2.4), add it to the sample cup by means of a dropper at this time ( **Caution**, see Note A2.5 and Note A2.6).

NOTE A2.3—After repeated use of the bomb for chlorine determination, a film may be noticed on the inner surface. This dullness should be removed by periodic polishing of the bomb. A satisfactory method for doing this is to rotate the bomb in a lathe at about 300 rpm and polish the inside surface with Grit No. 2/0 or equivalent paper coated with a light machine oil to prevent cutting, and then with a paste of grit-free chromic oxide and water. This procedure will remove all but very deep pits and put a high polish on the surface. Before using the bomb, it should be washed with soap and water to remove oil or paste left from the polishing operation. Bombs with porous or pitted surfaces should never be used because of the tendency to retain chlorine from sample to sample. **Caution:** Do not use more than 1 g total of sample and white oil or other chlorine-free combustible material.

NOTE A2.4—If the sample is not readily miscible with white oil, some other nonvolatile, chlorine-free combustible diluent may be employed in place of white oil. However, the combined weight of sample and nonvolatile diluent shall not exceed 1 g. Some solid additives are relatively insoluble, but may be satisfactorily burned when covered with a layer of white oil.

<sup>9</sup> *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 *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

NOTE A2.5—The practice of running alternately samples high and low in chlorine content should be avoided whenever possible. It is difficult to rinse the last traces of chlorine from the walls of the bomb and the tendency for residual chlorine to carry over from sample to sample has been observed in a number of laboratories. When a sample high in chlorine has preceded one low in chlorine content, the test on the low-chlorine sample should be repeated and one or both of the low values thus obtained should be considered suspect if they do not agree within the limits of repeatability of this method.

A2.5.2.2 *Addition of Oxygen*—Place the sample cup in position and arrange the nylon thread, or wisp of cotton so that the end dips into the sample. Assemble the bomb and tighten the cover securely. Admit oxygen (**Caution**, Note A2.6) slowly (to avoid blowing the sample from the cup) until a pressure is reached as indicated in Table A2.1.

NOTE A2.6—**Caution:** Do not add oxygen or ignite the sample if the bomb has been jarred, dropped, or tilted.

A2.5.2.3 *Combustion*—Immerse the bomb in a cold-water bath. Connect the terminals to the open electrical circuit. Close the circuit to ignite the sample. Remove the bomb from the bath after immersion for at least ten minutes. Release the pressure at a slow, uniform rate such that the operation requires not less than 1 min. Open the bomb and examine the contents. If traces of unburned oil or sooty deposits are found, discard the determination, and thoroughly clean the bomb before again putting it in use (Note A2.3).

## A2.6 Analysis, Method A, Potentiometric Titration Procedure

### A2.6.1 Apparatus:

A2.6.1.1 *Silver Billet Electrode.*

A2.6.1.2 *Glass Electrode, pH measurement type.*

A2.6.1.3 *Buret, 25-mL capacity, 0.05-mL graduations.*

A2.6.1.4 *Millivolt Meter, or expanded scale pH meter capable of measuring 0 to 220 mV.*

NOTE A2.7—An automatic titrator is highly recommended in place of items A2.6.1.3 and A2.6.1.4. Repeatability and sensitivity of the method are much enhanced by the automatic equipment while much tedious effort is avoided.

### A2.6.2 Reagents and Materials:

A2.6.2.1 *Acetone, chlorine-free.*

A2.6.2.2 *Methanol, chlorine-free.*

A2.6.2.3 *Silver Nitrate Solution (0.0282 N)*—Dissolve  $4.7910 \pm 0.0005$  g of silver nitrate ( $\text{AgNO}_3$ ) in water and dilute to 1 L.

A2.6.2.4 *Sodium Chloride Solution (0.0282 N)*—Dry a few grams of sodium chloride ( $\text{NaCl}$ ) for 2 h at 130 to 150°C, weigh out  $1.6480 \pm 0.0005$  g of the dried  $\text{NaCl}$ , dissolve in water, and dilute to 1 L.

A2.6.2.5 *Sulfuric Acid (1 + 2)*—Mix 1 volume of concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ , sp. gr 1.84) with 2 volumes of water.

A2.6.3 *Collection of Chlorine Solution*—Remove the sample cup with clean forceps and place in a 400-mL beaker. Wash down the walls of the bomb shell with a fine stream of methanol from a wash bottle, and pour the washings into the beaker. Rinse any residue into the beaker. Next, rinse the bomb cover and terminals into the beaker. Finally, rinse both inside and outside of the sample crucible into the beaker. Washings should equal but not exceed 100 mL. Add methanol to make 100 mL.

A2.6.4 *Determination of Chlorine*—Add 5 mL of  $\text{H}_2\text{SO}_4$  (1:2) to acidify the solution (solution should be acid to litmus and clear of white  $\text{Na}_2\text{CO}_3$  precipitate). Add 100 mL of acetone. Place the electrodes in the solution, start the stirrer (if mechanical stirrer is to be used), and begin titration. If titration is manual, set the pH meter on the expanded millivolt scale and note the reading. Add exactly 0.1 mL of  $\text{AgNO}_3$  solution from the buret. Allow a few seconds stirring; then record the new millivolt reading. Subtract the second reading from the first. Continue the titration, noting each amount of  $\text{AgNO}_3$  solution and the amount of difference between the present reading and the last reading. Continue adding 0.1-mL increments, making readings and determining differences between readings until a maximum difference between readings is obtained. The total amount of  $\text{AgNO}_3$  solution required to produce this maximum differential is the end point. Automatic titrators continuously stir the sample, add titrant, measure the potential difference, calculate the differential, and plot the differential on a chart. The maximum differential is taken as the end point.

NOTE A2.8—For maximum sensitivity, 0.00282 N  $\text{AgNO}_3$  solution may be used with the automatic titrator. This dilute reagent should not be used with large samples or where chlorine content may be over 0.1 % since these tests will cause end points of 10 mL or higher. The large amount of water used in such titrations reduces the differential between readings, making the end point very difficult to detect. For chlorine contents over 1 % in samples of 0.8 g or larger, 0.282 N  $\text{AgNO}_3$  solution will be required to avoid exceeding the 10-mL water dilution limit.

**TABLE A2.1 Gage Pressures**

Capacity of Bomb, mL	Gage Pressure, atm (MPa)	
	min <sup>A</sup>	max
300 to 350	38 (3.85)	40 (4.05)
350 to 400	35 (3.55)	37 (3.75)
400 to 450	30 (3.04)	32 (3.24)
450 to 500	27 (2.74)	29 (2.94)

<sup>A</sup> The minimum pressures are specified to provide sufficient oxygen for complete combustion and the maximum pressures present a safety requirement.

A2.6.5 *Blank*—Make blank determinations with the amount of white oil used but omitting the sample. (Liquid samples normally require only 0.15 to 0.25 g of white oil while solids require 0.7 to 0.8 g.) Follow normal procedure, making two or three test runs to be sure the results are within the limits of repeatability for the test. Repeat this blank procedure whenever new batches of reagents or white oil are used. The purpose of the blank run is to measure the chlorine in the white oil, the reagents, and that introduced by contamination.

A2.6.6 *Standardization*— Silver nitrate solutions are not permanently stable, so the true activity should be checked when the solution is first made up and then periodically during the life of the solution. This is done by titration of a known NaCl solution as follows: Prepare a mixture of the amounts of the chemicals (Na<sub>2</sub>CO<sub>3</sub> solution, H<sub>2</sub>SO<sub>4</sub> solution, acetone, and methanol) specified for the test. Pipet in 5.0 mL of 0.0282- *N* NaCl solution and titrate to the end point. Prepare and titrate a similar mixture of all the chemicals except the NaCl solution, thus obtaining a reagent blank reading. Calculate the normality of the AgNO<sub>3</sub> solution as follows:

$$N_{\text{AgNO}_3} = \frac{5.0 \times N_{\text{NaCl}}}{V_A - V_B} \quad (\text{A2.1})$$

where:

- $N_{\text{AgNO}_3}$  = normality of the AgNO<sub>3</sub> solution,
- $N_{\text{NaCl}}$  = normality of the NaCl solution,
- $V_A$  = millilitres of AgNO<sub>3</sub> solution used for the titration including the NaCl solution, and
- $V_B$  = millilitres of AgNO<sub>3</sub> solution used for the titration of the reagents only.

A2.6.7 *Calculation*— Calculate the chlorine content of the sample as follows:

$$\text{Chlorine, weight \%} = \frac{(V_S - V_B) \times N \times 3.545}{W} \quad (\text{A2.2})$$

where:

- $V_S$  = millilitres of AgNO<sub>3</sub> solution used by the sample,
- $V_B$  = millilitres of AgNO<sub>3</sub> solution used by the blank,
- $N$  = normality of the AgNO<sub>3</sub> solution, and
- $W$  = grams of sample used.

A2.6.8 *Precision and Accuracy*:

A2.6.8.1 The following criteria should be used for judging the acceptability of results:

A2.6.8.1.1 *Repeatability*— Results by the same analyst should not be considered suspect unless they differ by more than 0.006 % or 10.5 % of the value determined, whichever is higher.

A2.6.8.1.2 *Reproducibility*— Results by different laboratories should not be considered suspect unless they differ by more than 0.013 % or 21.3 % of the value detected, whichever is higher.

A2.6.8.1.3 *Accuracy*—The average recovery of the method is 86 % to 89 % of the actual amount present.

## A2.7 Analysis, Method B, Coulometric Titration

A2.7.1 *Apparatus*:

A2.7.1.1 *Coulometric Chloride Titrator* .

A2.7.1.2 *Beakers*, two, 100-mL, or glazed crucibles (preferably with 1½ in.-outside diameter bottom).

A2.7.1.3 *Refrigerator*.

A2.7.2 *Reagents*:

A2.7.2.1 *Acetic Acid, Glacial*.

A2.7.2.2 *Dry Gelatin Mixture*.<sup>10</sup>

A2.7.2.3 *Nitric Acid*.

A2.7.2.4 *Sodium Chloride Solution*—100 meq C/1. Dry a quantity of NaCl for 2 h at 130 to 150°C. Weigh out 5.8440 ± 0.0005 g of dried NaCl in a closed container, dissolve in water, and dilute to 1 L.

A2.7.3 *Reagent Preparation*:

NOTE A2.9—The normal reagent preparation process has been slightly changed, due to the interference from the 50 mL of water required to wash the bomb. This modified process eliminates the interference and does not alter the quality of the titration.

A2.7.3.1 *Gelatin Solution*—A typical preparation is: Add approximately 1 L of hot distilled or deionized water to the 6.2 g of dry gelatin mixture contained in one vial supplied by the equipment manufacturer. Gently heat with continuous mixing until the gelatin is completely dissolved.

A2.7.3.2 Divide into aliquots each sufficient for one day's analyses. (Thirty millilitres is enough for approximately eleven titrations.) Keep the remainder in a refrigerator, but do not freeze. The solution will keep for about 6 months in the refrigerator. When ready to use, immerse the day's aliquot in hot water to liquefy the gelatin.

<sup>10</sup> May be purchased from the equipment supplier. A typical mixture consists of 6 g of gelatin powder, 0.1 g of thymol blue, water-soluble, and 0.1 g of thymol, reagent grade, crystal.



A2.7.3.3 *Glacial Acetic Acid-Nitric Acid Solution*—A typical ratio is 12.5 to 1 (12.5 parts CH<sub>3</sub>COOH to 1 part HNO<sub>3</sub>).

A2.7.3.4 Mix enough gelatin solution and of acetic acid-nitric acid mixture for one titration. (A typical mixture is 2.5 mL of gelatin solution and 5.4 mL of acetic-nitric acid mixture.)

NOTE A2.10—The solution may be premixed in a larger quantity for convenience, but may not be useable after 24 h.

A2.7.3.5 Run at least three blank values and take an average according to the operating manual of the titrator. Determine separate blanks for both 5 drops of mineral oil and 20 drops of mineral oil.

A2.7.4 *Titration:*

A2.7.4.1 Weigh to the nearest 0.1 g and record the weight of the 100-mL beaker.

A2.7.4.2 Remove the sample crucible from the cover assembly support ring using a clean forceps, and, using a wash bottle, rinse both the inside and the outside with water into the 100-mL beaker.

A2.7.4.3 Empty the bomb shell into the 100-mL beaker. Wash down the sides of the bomb shell with water, using a wash bottle.

A2.7.4.4 Remove the cover assembly from the cover assembly support, and, using the wash bottle, rinse the under side, the platinum wire, and the terminals into the same 100-mL beaker. The total amount of washings should be 50 ± 1 g.

A2.7.4.5 Add specified amounts of gelatin mixture and acetic acid-nitric acid mixture, or gelatin mix-acetic acid-nitric acid mixture, if this was premixed, into the 100-mL beaker that contains the 50 g of washings including the decomposed sample.

A2.7.4.6 Titrate using a coulometric titrimeter, according to operating manual procedure.

A2.7.5 *Calculations*— Calculate the chloride ion concentration in the sample as follows:

$$\text{Chlorine, weight \%} = \frac{(P - B) \times M}{W} \quad (\text{A2.3})$$

where:

*P* = counter reading obtained with the sample,

*B* = average counter reading obtained with average of the three blank readings,

*M* = standardization constant. This is dependent on the instrument range setting in use and the reading obtained with a known amount of the 100 meq of Cl per litre of solution, and

*W* = weight of sample used, g.

A2.7.6 *Precision and Accuracy:*

A2.7.6.1 Duplicate results by the same operator can be expected to exhibit the following relative standard deviations:

Approximate % Chlorine	RSD, %
1.0 and above	0.10
0.1	2.5
0.003	5.9

A2.7.6.2 The method can be expected to report values that vary from the true value by the following amounts:

0.1 % chlorine and above	±2%
0.001 to 0.01 % chlorine	±9%

A2.7.6.3 If bromine is present, 36.5 % of the true amount will be reported. If iodine is present, 20.7 % of the true amount will be reported. Fluorine will not be detected.

### A3. METHOD FOR MEASURING TOTAL FLUORINE CONTENT IN COMBUSTIBLE LIQUID PENETRANT MATERIALS

#### A3.1 Scope and Application

A3.1.1 This method covers the determination of fluorine in combustible liquid penetrant materials, liquid or solid, that do not contain appreciable amounts of interfering elements, or have any insoluble residue after combustion. Its range of applicability is 1 to 200 000 ppm.

A3.1.2 The measure of the fluorine content employs the fluoride selective ion electrode.

#### A3.2 Summary of Method

A3.2.1 The sample is oxidized by combustion in a bomb containing oxygen under pressure (**Caution**, see A3.2.1.1). The fluorine compounds thus liberated are absorbed in a sodium citrate solution and the amount of fluorine present is determined potentiometrically through the use of a fluoride selective ion electrode.

A3.2.1.1 *Safety*—Strict adherence to all of the provisions prescribed hereinafter ensures against explosive rupture of the bomb, or a blow-out, provided the bomb is of proper design and construction and in good mechanical condition. It is desirable, however, that the bomb be enclosed in a shield of steel plate at least ½ in. (12.7 mm) thick, or equivalent protection be provided against unforeseeable contingencies.

### A3.3 Interferences

A3.3.1 Silicon, calcium, aluminum, magnesium, and other metals forming precipitates with fluoride ion will interfere if they are present in sufficient concentration to exceed the solubility of their respective fluorides. Insoluble residue after combustion will entrain fluorine even if otherwise soluble.

### A3.4 Apparatus

A3.4.1 *Bomb*, having a capacity of not less than 300 mL, so constructed that it will not leak during the test, and that quantitative recovery of the liquids from the bomb may be readily achieved. The inner surface of the bomb may be made of stainless steel or any other material that will not be affected by the combustion process or products. Materials used in the bomb assembly, such as the head gasket and leadwire insulation, shall be resistant to heat and chemical action, and shall not undergo any reaction that will affect the fluorine content of the liquid in the bomb.

A3.4.2 *Sample Cup*, nickel, 20 mm in outside diameter at the bottom, 28 mm in outside diameter at the top, and 16 mm in height; or platinum, 24 mm in outside diameter at the bottom, 27 mm in outside diameter at the top, 12 mm in height, and weighing 10 to 11 g.

A3.4.3 *Firing Wire*, platinum, approximately No. 26 B & S gage.

A3.4.4 *Ignition Circuit* (Note A3.1), capable of supplying sufficient current to ignite the nylon thread or cotton wicking without melting the wire.

NOTE A3.1—**Caution:** The switch in the ignition circuit shall be of a type that remains open, except when held in closed position by the operator.

A3.4.5 *Nylon Sewing Thread*, or *Cotton Wicking*, white.

A3.4.6 *Funnel*, polypropylene (Note A3.2).

A3.4.7 *Volumetric Flask*, polypropylene, 100-mL (Note A3.2).

A3.4.8 *Beaker*, polypropylene, 150-mL (Note A3.2).

A3.4.9 *Pipet*, 100- $\mu$ L, Eppendorf-type (Note A3.2).

A3.4.10 *Magnetic Stirrer* and TFE-coated magnetic stirring bar.

A3.4.11 *Fluoride Specific Ion Electrode* and suitable reference electrode.

A3.4.12 *Millivolt Meter* capable of measuring to 0.1 mV.

NOTE A3.2—Glassware should never be used to handle a fluoride solution as it will remove fluoride ions from solution or on subsequent use carry fluoride ion from a concentrated solution to one more dilute.

### A3.5 Reagents

A3.5.1 *Purity of Reagents*—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.<sup>9</sup> 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.

A3.5.2 *Purity of Water*— Unless otherwise indicated, all references to water shall be understood to mean Type I reagent water conforming to Specification D 1193.

A3.5.3 *Fluoride Solution, Stock (2000 ppm)*—Dissolve  $4.4200 \pm 0.0005$  g of predried (at 130 to 150°C for 1 h, then cooled in a desiccator) sodium fluoride in distilled water and dilute to 1 L.

A3.5.4 *Oxygen*, free of combustible material and halogen compounds, available at a pressure of 40 atm (4.05 MPa).

A3.5.5 *Sodium Citrate Solution*—Dissolve 27 g of sodium citrate dihydrate in water and dilute to 1 L.

A3.5.6 *Sodium Hydroxide Solution (5 N)*—Dissolve 200 g of sodium hydroxide (NaOH) pellets in water and dilute to 1 L; store in a polyethylene container.

A3.5.7 *Wash Solution (Modified TISAB, Total Ionic Strength Adjustment Buffer)*—To 300 mL of distilled water, add 32 mL of glacial acetic acid, 6.6 g of sodium citrate dihydrate, and 32.15 g of sodium chloride. Stir to dissolve and then adjust the pH to 5.3 using 5 N NaOH solution. Cool and dilute to 1 L.

A3.5.8 *White Oil*, refined.

### A3.6 Decomposition Procedure

A3.6.1 *Preparation of Bomb and Sample* —Cut a piece of firing wire approximately 100 mm in length. Coil the middle section (about 20 mm) and attach the free ends to the terminals. Arrange the coil so that it will be above and to one side of the sample cup. Place 10 mL of sodium citrate solution in the bomb, place the cover on the bomb, and vigorously shake for 15 s to distribute the solution over the inside of the bomb. Open the bomb, place the sample-filled sample cup in the terminal holder, and insert a short length of thread between the firing wire and the sample. The sample weight used should not exceed 1 g. If the sample is a solid, add a few drops of white oil at this time to ensure ignition of the sample.

NOTE A3.3—Use of sample weights containing over 20 mg of chlorine may cause corrosion of the bomb. To avoid this it is recommended that for samples containing over 2 % chlorine, the sample weight be based on the following table:

Chlorine Content, %	Sample weight, g	White Oil weight, g
2 to 5	0.4	0.4
5 to 10	0.2	0.6
10 to 20	0.1	0.7
20 to 50	0.05	0.7

**Caution:** Do not use more than 1 g total of sample and white oil or other fluorine-free combustible material.

A3.6.2 *Addition of Oxygen*—Place the sample cup in position and arrange the nylon thread, or wisp of cotton so that the end dips into the sample. Assemble the bomb and tighten the cover securely. Admit oxygen (**Caution**, Note A3.4) slowly (to avoid blowing the sample from the cup) until a pressure is reached as indicated in Table A3.1.

NOTE A3.4—**Caution:** Do not add oxygen or ignite the sample if the bomb has been jarred, dropped, or tilted.

A3.6.3 *Combustion*— Immerse the bomb in a cold-water bath. Connect the terminals to the open electrical circuit. Close the circuit to ignite the sample. Remove the bomb from the bath after immersion for at least 10 min. Release the pressure at a slow, uniform rate such that the operation requires not less than 1 min. Open the bomb and examine the contents. If traces of unburned oil or sooty deposits are found, discard the determination, and thoroughly clean the bomb before again putting it in use.

A3.6.4 *Collection of Fluorine Solution* —Remove the sample cup with clean forceps and rinse with wash solution into a 100-mL volumetric flask. Rinse the walls of the bomb shell with a fine stream of wash solution from a wash bottle, and add the washings to the flask. Next, rinse the bomb cover and terminals into the volumetric flask. Finally, add wash solution to bring the contents of the flask to the line.

### A3.7 Procedure

A3.7.1 Ascertain the slope (millivolts per ten-fold change in concentration) of the electrode as described by the manufacturer.

A3.7.2 Obtain a blank solution by performing the procedure without a sample.

A3.7.3 Immerse the fluoride and reference electrodes in solutions and obtain the equilibrium reading to 0.1 mV. (The condition of the electrode determines the length of time necessary to reach equilibrium. This may be as little as 5 min or as much as 20 min.)

A3.7.4 Add 100  $\mu$ L of stock fluoride solution and obtain the reading after the same length of time necessary for A3.7.3.

### A3.8 Calculation

A3.8.1 Calculate the fluorine content of the sample as follows:

$$\text{Fluorine, ppm} = \frac{\left[ \frac{2 \times 10^{-4}}{10\Delta E_1/S - 1} - \frac{2 \times 10^{-4}}{10\Delta E_2/S - 1} \right]}{W} \times 10^6 \quad (\text{A3.1})$$

where:

$\Delta E_1$  = millivolt change in sample solution on addition of 100  $\mu$ L of stock fluoride solution,

$\Delta E_2$  = millivolt change in blank solution on addition of 100  $\mu$ L of the stock fluoride solution,

$S$  = slope of fluoride electrode as determined in A3.7.1, and

$W$  = grams of sample.

### A3.9 Precision and Bias

A3.9.1 *Repeatability*— The results of two determinations by the same analyst should not be considered suspect unless they differ by more than 1.1 ppm (0.00011 %) or 8.0 % of the amount detected, whichever is greater.

A3.9.2 *Reproducibility*— The results of two determinations by different laboratories should not be considered suspect unless they differ by 6.7 ppm or 129.0 % of the amount detected, whichever is greater.

A3.9.3 *Bias*—The average recovery of the method is 62 to 64 % of the amount actually present although 83 to 85 % recoveries can be expected with proper technique.

**TABLE A3.1 Gage Pressures**

Capacity of Bomb, mL	Gage Pressure atm (MPa)	
	min <sup>A</sup>	max
300 to 350	38	40
350 to 400	35	37
400 to 450	30	32
450 to 500	27	29

<sup>A</sup> The minimum pressures are specified to provide sufficient oxygen for complete combustion and the maximum pressures present a safety requirement.

## A4. DETERMINATION OF ANIONS BY ION CHROMATOGRAPHY WITH CONDUCTIVITY MEASUREMENT

### A4.1 Scope and Application

A4.1.1 This method is condensed from ASTM procedures and APHA Method 429 and optimized for the analysis of detrimental substances in organic based materials. It provides a single instrumental technique for rapid, sequential measurement of common anions such as bromide, chloride, fluoride, nitrate, nitrite, phosphate, and sulfate.

### A4.2 Summary of Method

A4.2.1 The material must be put in the form of an aqueous solution before analysis can be attempted. The sample is oxidized by combustion in a bomb containing oxygen under pressure. The products liberated are absorbed in the eluant present in the bomb at the time of ignition. This solution is washed from the bomb, filtered, and diluted to a known volume.

A4.2.1.1 A filtered aliquot of sample is injected into a stream of carbonate-bicarbonate eluant and passed through a series of ion exchangers. The anions of interest are separated on the basis of their relative affinities for a low capacity, strongly basic anion exchanger (guard and separator column). The separated anions are directed onto a strongly acidic cation exchanger (suppressor column) where they are converted to their highly conductive acid form and the carbonate-bicarbonate eluant is converted to weakly conductive carbonic acid. The separated anions in their acid form are measured by conductivity. They are identified on the basis of retention time as compared to standards. Quantitation is by measurement of peak area or peak height. Blanks are prepared and analyzed in a similar fashion.

A4.2.2 *Interferences*— Any substance that has a retention time coinciding with that of any anion to be determined will interfere. For example, relatively high concentrations of low-molecular-weight organic acids interfere with the determination of chloride and fluoride. A high concentration of any one ion also interferes with the resolution of others. Sample dilution overcomes many interferences. To resolve uncertainties of identification or quantitation use the method of known additions. Spurious peaks may result from contaminants in reagent water, glassware, or sample processing apparatus. Because small sample volumes are used, scrupulously avoid contamination.

A4.2.3 *Minimum Detectable Concentration* —The minimum detectable concentration of an anion is a function of sample size and conductivity scale used. Generally, minimum detectable concentrations are in the range of 0.05 mg/L for  $F^-$  and 0.1 mg/L for  $Br^-$ ,  $Cl^-$ ,  $NO_3^-$ ,  $NO_2^-$ ,  $PO_4^{3-}$ , and  $SO_4^{2-}$  with a 100- $\mu$ L sample loop and a 10- $\mu$ mho full-scale setting on the conductivity detector. Similar values may be achieved by using a higher scale setting and an electronic integrator.

### A4.3 Apparatus

A4.3.1 *Bomb*, having a capacity of not less than 300 mL, so constructed that it will not leak during the test, and that quantitative recovery of the liquids from the bomb may be readily achieved. The inner surface of the bomb may be made of stainless steel or any other material that will not be affected by the combustion process or products. Materials used in the bomb assembly, such as the head gasket and leadwire insulation, shall be resistant to heat and chemical action, and shall not undergo any reaction that will affect the chlorine content of the liquid in the bomb.

A4.3.2 *Sample Cup*, platinum, 24 mm in outside diameter at the bottom, 27 mm in outside diameter at the top, 12 mm in height outside, and weighing 10 to 11 g; opaque fused silica, wide-form with an outside diameter of 29 mm at the top, a height of 19 mm, and a 5-mL capacity (Note A4.1), or nickel (Kawin capsule form), top diameter of 28 mm, 15 mm in height, and 5-mL capacity.

NOTE A4.1—Fused silica crucibles are much more economical and longer lasting than platinum. After each use, they should be scrubbed out with fine, wet emery cloth, heated to dull red heat over a burner, soaked in hot water for 1 h then dried and stored in a desiccator before reuse.

A4.3.3 *Firing Wire*, platinum, approximately No. 26 B and S gage.

A4.3.4 *Ignition Circuit* (Note A4.2), capable of supplying sufficient current to ignite the nylon thread or cotton wicking without melting the wire.

NOTE A4.2—**Caution:** The switch in the ignition circuit shall be of a type that remains open, except when held in closed position by the operator.

A4.3.5 *Nylon Sewing Thread*, or *Cotton Wicking*, white.

A4.3.6 *Ion Chromatograph*, including an injection valve, a sample loop, guard, separator, and suppressor columns, a temperature-compensated small-volume conductivity cell (6  $\mu$ L or less), and a strip chart recorder capable of full-scale response of 2 s or less. An electronic peak integrator is optional. The ion chromatograph shall be capable of delivering 2 to 5 mL eluant/min at a pressure of 1400 to 6900 kPa.

A4.3.7 *Anion Separator Column*, with styrene divinylbenzene-based low-capacity pellicular anion-exchange resin capable of resolving  $Br^-$ ,  $Cl^-$ ,  $F^-$ ,  $NO_3^-$ ,  $NO_2^-$ ,  $PO_4^{3-}$ , and  $SO_4^{2-}$ ; 4  $\times$  250 mm.

A4.3.8 *Guard Column*, identical to separator column except 4  $\times$  50 mm, to protect separator column from fouling by particulates or organics.

A4.3.9 *Suppressor Column*, high-capacity cation-exchange resin capable of converting eluant and separated anions to their acid forms.

A4.3.10 *Syringe*, minimum capacity of 2 mL and equipped with a male pressure fitting.

## A4.4 Reagents

A4.4.1 *Purity of Reagents*—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.<sup>9</sup> Other grades may be used provided it is first ascertained that the reagent has sufficiently high purity to permit its use without lessening the accuracy of the determination.

A4.4.2 *Deionized or Distilled Water*, free from interferences at the minimum detection limit of each constituent and filtered through a 0.2- $\mu$ m membrane filter to avoid plugging columns.

A4.4.3 *Eluant Solution*, sodium bicarbonate-sodium carbonate, 0.003M NaHCO<sub>3</sub>-0.0024M Na<sub>2</sub>CO<sub>3</sub>: dissolve 1.008 g NaHCO<sub>3</sub> and 1.0176 g Na<sub>2</sub>CO<sub>3</sub> in water and dilute to 4 L.

A4.4.4 *Regenerant Solution 1*, H<sub>2</sub>SO<sub>4</sub>, 1 N, use this regenerant when suppressor is not a continuously regenerated one.

A4.4.5 *Regenerant Solution 2*, H<sub>2</sub>SO<sub>4</sub>, 0.025 N, dilute 2.8 mL conc H<sub>2</sub>SO<sub>4</sub> to 4 L or 100 mL regenerant solution 1 to 4 L. Use this regenerant with continuous regeneration fiber suppressor system.

A4.4.6 *Standard Anion Solutions*, 1000 mg/L, prepare a series of standard anion solutions by weighing the indicated amount of salt, dried to a constant weight at 105°C, to 1000 mL. Store in plastic bottles in a refrigerator; these solutions are stable for at least one month.

Anion	Salt	Amount, g/L
Cl <sup>-</sup>	NaCl	1.6485
F <sup>-</sup>	NaF	2.2100
Br <sup>-</sup>	NaBr	1.2876
NO <sub>3</sub> <sup>-</sup>	NaNO <sub>3</sub>	1.3707
NO <sub>2</sub> <sup>-</sup>	NaNO <sub>2</sub>	1.4998
PO <sub>4</sub> <sup>3-</sup>	KH <sub>2</sub> PO <sub>4</sub>	1.4330
SO <sub>4</sub> <sup>2-</sup>	K <sub>2</sub> SO <sub>4</sub>	1.8141

A4.4.7 *Combined Working Standard Solution, High Range*—Combine 10 mL of the Cl<sup>-</sup>, F<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, and PO<sub>4</sub><sup>3-</sup> standard anion solutions, 1 mL of the Br<sup>-</sup>, and 100 mL of the SO<sub>4</sub><sup>2-</sup> standard solutions, dilute to 1000 mL, and store in a plastic bottle protected from light; contains 10 mg/L each of Cl<sup>-</sup>, F<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, and PO<sub>4</sub><sup>3-</sup>, 1 mg Br<sup>-</sup>/L, and 100 mg SO<sub>4</sub><sup>2-</sup>/L. Prepare fresh daily.

A4.4.8 *Combined Working Standard Solution, Low Range*—Dilute 100 mL combined working standard solution, high range, to 1000 mL and store in a plastic bottle protected from light; contains 1.0 mg/L each Cl<sup>-</sup>, F<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, and PO<sub>4</sub><sup>3-</sup>, 0.1 mg Br<sup>-</sup>/L, and 10 mg SO<sub>4</sub><sup>2-</sup>/L. Prepare fresh daily.

A4.4.9 *Alternative Combined Working Standard Solutions*—Prepare appropriate combinations according to anion concentration to be determined. If NO<sub>2</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup> are not included, the combined working standard is stable for one month.

## A4.5 Decomposition Procedure

A4.5.1 *Preparation of Bomb and Sample*—Cut a piece of firing wire approximately 100 mm in length. Coil the middle section (about 20 mm) and attach the free ends to the terminals. Arrange the coil so that it will be above and to one side of the sample cup. Place 5 mL of Na<sub>2</sub>CO<sub>3</sub>/NaHCO<sub>3</sub> solution in the bomb, place the cover on the bomb, and vigorously shake for 15 s to distribute the solution over the inside of the bomb. Open the bomb, place the sample-filled sample cup in the terminal holder, and insert a short length of thread between the firing wire and the sample. The sample weight used should not exceed 1 g. If the sample is a solid, add a few drops of white oil at this time to ensure ignition of the sample.

NOTE A4.3—Use of sample weights containing over 20 mg of chlorine may cause corrosion of the bomb. To avoid this it is recommended that for samples containing over 2 % chlorine, the sample weight be based on the following:

Chlorine content, %	Sample weight, g	White Oil weight, g
2 to 5	0.4	0.4
5 to 10	0.2	0.6
10 to 20	0.1	0.7
20 to 50	0.05	0.7

**CAUTION:** Do not use more than 1 g total of sample and white oil or other fluorine-free combustible material.

A4.5.2 *Addition of Oxygen*—Place the sample cup in position and arrange the nylon thread, or wisp of cotton so that the end dips into the sample. Assemble the bomb and tighten the cover securely. Admit oxygen (**Caution**, Note A4.4) slowly (to avoid blowing the sample from the cup) until a pressure is reached as indicated in Table A4.1.

NOTE A4.4—**Caution:** Do not add oxygen or ignite the sample if the bomb has been jarred, dropped, or tilted.

A4.5.3 *Combustion*—Immerse the bomb in a cold-water bath. Connect the terminals to the open electrical circuit. Close the circuit to ignite the sample. Remove the bomb from the bath after immersion for at least 10 min. Release the pressure at a slow, uniform rate such that the operation requires not less than 1 min. Open the bomb and examine the contents. If traces of unburned oil or sooty deposits are found, discard the determination, and thoroughly clean the bomb before again putting it in use.

A4.5.4 *Collection of Solution*—Remove the sample cup with clean forceps and rinse with deionized water and filter the

**TABLE A4.1 Gage Pressures**

Capacity of Bomb, mL	Gage Pressures, atm	
	mm <sup>A</sup>	max
300 to 350	38	40
350 to 400	35	37
400 to 450	30	32
450 to 500	27	29

<sup>A</sup> The minimum pressures are specified to provide sufficient oxygen for complete combustion and the maximum pressures present a safety requirement.

washings into a 100-mL volumetric flask. Rinse the walls of the bomb shell with a fine stream of deionized water from a wash bottle, and add the washings through the filter paper to the flask. Next, rinse the bomb cover and terminals and add the washings through the filter into the volumetric flask. Finally, add deionized water to bring the contents of the flask to the line. Use aliquots of this solution for the ion chromatography (IC) analysis.

### A4.6 Procedure

A4.6.1 *System Equilibration*—Turn on ion chromatograph and adjust eluant flow rate to approximate the separation achieved in Fig. A4.1 (2 to 3 mL/min). Adjust detector to desired setting (usually 10 μmho) and let system come to equilibrium (15 to 20 min). A stable base line indicates equilibrium conditions. Adjust detector offset to zero-out eluant conductivity; with the fiber suppressor adjust the regeneration flow rate to maintain stability, usually 2.5 to 3 mL/min.

A4.6.1.1 Set up the ion chromatograph in accordance with the manufacturer’s instructions.

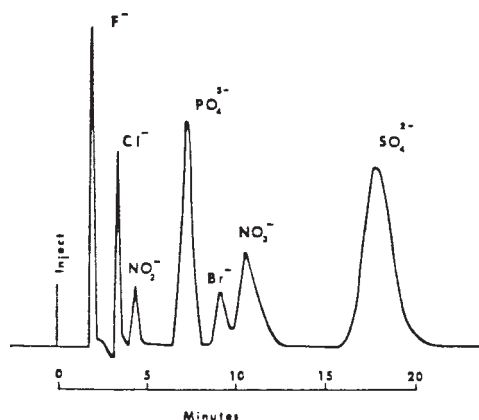
A4.6.2 *Calibration*—Inject standards containing a single anion or a mixture and determine approximate retention times. Observed times vary with conditions but if standard eluant and anion separator column are used, retention always is in the order F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>. Inject at least three different concentrations for each anion to be measured and construct a calibration curve by plotting peak height or area against concentration on linear graph paper. Recalibrate whenever the detector setting is changed. With a system requiring suppressor regeneration, NO<sub>2</sub><sup>-</sup> interaction with the suppressor may lead to erroneous NO<sub>2</sub><sup>-</sup> results; make this determination only when the suppressor is at the same stage of exhaustion as during standardization or recalibrate frequently. In this type of system the water dip (see Note A4.4) may shift slightly during suppressor exhaustion and with a fast run column this may lead to slight interference for F<sup>-</sup> or Cl<sup>-</sup>. To eliminate this interference, analyze standards that bracket the expected result or eliminate the water dip by diluting the sample with eluant or by adding concentrated eluant to the sample to give the same HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup> concentration as in the eluant. If sample adjustments are made, adjust standards and blanks identically.

NOTE A4.5—Water dip occurs because water conductivity in sample is less than eluant conductivity (eluant is diluted by water).

A4.6.2.1 If linearity is established for a given detector setting, it is acceptable to calibrate with a single standard. Record the peak height or area and retention time to permit calculation of the calibration factor, F.

A4.6.3 *Sample Analysis*—Remove sample particulates, if necessary, by filtering through a prewashed 0.2-μm-pore-diam membrane filter. Using a prewashed syringe of 1 to 10 mL capacity equipped with a male luer fitting inject sample or standard. Inject enough sample to flush sample loop several times: for 0.1 mL sample loop inject at least 1 mL. Switch ion chromatograph from load to inject mode and record peak heights and retention times on strip chart recorder. After the last peak (SO<sub>4</sub><sup>2-</sup>) has appeared and the conductivity signal has returned to base line, another sample can be injected.

A4.6.4 *Regeneration*—For systems without fiber suppressor regenerate with 1 N H<sub>2</sub>SO<sub>4</sub> in accordance with the manufacturer’s instructions when the conductivity base line exceeds 300 μmho when the suppressor column is on line.



**FIG. A4.1 Typical Anion Profile**

**A4.7 Calculation**

A4.7.1 Calculate concentration of each anion, in mg/L, by referring to the appropriate calibration curve. Alternatively, when the response is shown to be linear, use the following equation:

$$C = H \times F \times D \quad (\text{A4.1})$$

where:

$C$  = mg anion/L,

$H$  = peak height or area,

$F$  = response factor – concentration of standard/height (or area) of standard, and

$D$  = dilution factor for those samples requiring dilution.

## A4.8 Precision and Bias

A4.8.1 Samples of reagent water to which were added the common anions were analyzed in 15 laboratories with the results shown in Table A4.2.

*ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.*

*This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.*

*This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org).*

**TABLE A4.2 Precision and Accuracy Observed for Anions at Various Concentration Levels in Reagent Water**

Anion	Amount Added, mg/L	Amount Found, mg/L	Overall Precision, mg/L	Single-Operator Precision, mg/L	Significant Bias 95 % Level
F <sup>-</sup>	0.48	0.49	0.05	0.03	No
F <sup>-</sup>	4.84	4.64	0.52	0.46	No
Cl	0.76	0.86	0.38	0.11	No
Cl <sup>-</sup>	17	17.2	0.82	0.43	No
Cl	455	471	46	13	No
NO <sub>2</sub>	0.45	0.09	0.09	0.04	Yes, neg
NO <sub>2</sub>	21.8	19.4	1.9	1.3	Yes, neg
Br <sup>-</sup>	0.25	0.25	0.04	0.02	No
Br <sup>-</sup>	13.7	12.9	1.0	0.6	No
PO <sub>4</sub> <sup>3-</sup>	0.18	0.10	0.06	0.03	Yes, neg
PO <sub>4</sub> <sup>3-</sup>	0.49	0.34	0.15	0.17	Yes, neg
NO <sub>3</sub> <sup>-</sup>	0.50	0.33	0.16	0.03	No
NO <sub>3</sub> <sup>-</sup>	15.1	14.8	1.15	0.9	No
SO <sub>4</sub> <sup>2-</sup>	0.51	0.52	0.07	0.03	No
SO <sub>4</sub> <sup>2-</sup>	43.7	43.5	2.5	2.2	No