



Designation: ~~D513 – 11~~<sup>ε1</sup> D513 – 16

# Standard Test Methods for Total and Dissolved Carbon Dioxide in Water<sup>1</sup>

This standard is issued under the fixed designation D513; 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 reappraisal. A superscript epsilon (ε) indicates an editorial change since the last revision or reappraisal.

~~ε<sup>1</sup> NOTE—This test method was changed editorially in February 2012.~~

## 1. Scope\*

1.1 These test methods cover the measurement of total or dissolved carbon dioxide present as carbon dioxide (CO<sub>2</sub>), carbonic acid, bicarbonate ion, and carbonate ion in water:

	Range	Sections
Test Method A (Gas Sensing Electrode)	2 to 800 mg/L	8 to 15
Test Method B (CO <sub>2</sub> Evolution, Coulometric Titration)	5 to 800 mg/L	16 to 24

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Test Method A (Gas Sensing Electrode)	2 to 800 mg/L	8 to 15
Test Method B (CO <sub>2</sub> Evolution, Coulometric Titration)	5 to 800 mg/L	16 to 24

1.2 Carbon dioxide may also be detected from carbonates present in particulates in samples.

1.3 Test Method A is applicable to various natural waters and brines.

1.4 Test Method B is applicable to natural waters, brines, and various industrial waters as delineated in 16.4.

1.5 It is the user's responsibility to ensure the validity of these test methods on waters of untested matrices.

1.6 Several test methods were discontinued from this standard in 1988. Refer to Appendix X1 for historical information.

1.7 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.8 *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.*

## 2. Referenced Documents

2.1 ASTM Standards:<sup>2</sup>

[D1066 Practice for Sampling Steam](#)

[D1129 Terminology Relating to Water](#)

[D1193 Specification for Reagent Water](#)

[D1293 Test Methods for pH of Water](#)

[D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water](#)

[D3370 Practices for Sampling Water from Closed Conduits](#)

[D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis](#)

[E200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis](#)

## 3. Terminology

3.1 ~~Definitions~~ Definitions:—For

3.1.1 For definitions of terms used in this standard, refer to Terminology [D1129](#). ~~definitions of terms used in these test methods, refer to Terminology [D1129](#).~~

<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee [D19](#) on Water and are the direct responsibility of Subcommittee [D19.05](#) on Inorganic Constituents in Water.

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

\*A Summary of Changes section appears at the end of this standard

#### 4. Significance and Use

4.1 Carbon dioxide is a ~~major~~ respiration product of plants and animals and a decomposition product of organic matter and certain minerals. The atmosphere averages about 0.04 vol % of CO<sub>2</sub>. Surface waters generally contain less than 10 mg/L, except at local points of abnormal organic or mineral decomposition; however, underground water, particularly deep waters, may contain several hundred mg/L.

4.2 When dissolved in water, CO<sub>2</sub> contributes significantly to corrosion of water-handling systems. This is particularly troublesome in steam condensate systems. Loss of CO<sub>2</sub> from an aqueous system can disturb the carbonate equilibrium and result in calcite encrustation of confining surfaces. Scaling of water heaters is a good example. Because of the delicate balance between corrosion and encrustation tendencies, much care must be given to control of CO<sub>2</sub> and related species in water systems. Recarbonation of municipal supplies during final stages of softening and amine neutralization of steam condensate are applied for these purposes.

#### 5. Purity of Reagents

5.1 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.<sup>3</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.

5.2 Unless otherwise indicated, references to water shall be understood to mean water conforming to Type I of Specification **D1193**. Other reagent water types may be used provided it is first ascertained that the water is of sufficiently high purity to permit its use without adversely affecting the bias and precision of the test method. Additionally, for those test methods requiring water free of CO<sub>2</sub>, refer to **8.2** of Practice **E200**.

#### 6. Precautions

6.1 **Warning**—Carbon dioxide is easily lost from solution during transit and storage of samples. It is also possible for total CO<sub>2</sub> concentration to increase after sampling due to solution of finely divided calcium carbonate as a result of temperature or pressure changes.

#### 7. Sampling

7.1 Collect the sample in accordance with ~~Practices~~ **Practice D1066** and **Practices D3370**, as applicable.

7.2 Filter samples when they are collected if particulates are present that may contain carbonates if dissolved species only are to be determined. When aliquots of sample are taken from sample bottles containing particulates, the bottle must be shaken or otherwise homogenized to ensure a representative sample is taken. When particulates form in samples due to changes in temperature, pH, etc., after the sample has been collected, these particulates must be included in tests of the sample. Care must be used to avoid loss of CO<sub>2</sub> during any homogenization of filtration of samples. Do not filter samples unless it is required to remove potentially interfering particulates.

7.3 Use a hard, glass, chemically resistant bottle for collecting the sample.

7.4 Fill the sample bottle completely, with no air space remaining beneath the cap, and store the sample at a temperature below that at which it was collected until the determination is made.

### **TEST METHOD A—~~GAS SENSING ELECTRODE~~ SENSING ELECTRODE TEST METHOD**

#### 8. Scope

8.1 This test method determines total or dissolved carbon dioxide (**14.3**) present as CO<sub>2</sub>, carbonic acid, bicarbonate ion, and carbonate ion in water, within the interference constraints specified.

8.2 Samples containing 2 to 800 mg/L total CO<sub>2</sub> can be analyzed by this test method. The concentration range may be extended by dilution of an appropriate aliquot.

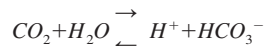
8.3 Samples should be analyzed immediately. If this is not possible, preserve by making them slightly alkaline (pH between 8 and 9) using carbonate-free NaOH solution and store them in a tightly capped vessel. The latter step prevents absorption of CO<sub>2</sub> from the air.

8.4 The precision and bias were obtained on reagent water and a water matrix of choice that included natural waters and brines. It is the responsibility of the analyst to determine the acceptability of this test method for the water being analyzed.

<sup>3</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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

## 9. Summary of Test Method

9.1 Carbon dioxide is liberated by acidification of the sample to pH 5.0. The carbon dioxide electrode uses a gas-permeable membrane to separate the sample solution from the electrode internal solution. Dissolved carbon dioxide in the sample solution diffuses through the membrane until an equilibrium is reached between the partial pressure of CO<sub>2</sub> in the sample solution and the CO<sub>2</sub> in the internal filling solution. In any given sample, the partial pressure of CO<sub>2</sub> will be proportional to the concentration of CO<sub>2</sub>. The diffusion of CO<sub>2</sub> across the membrane affects the concentration of hydrogen ions in the internal filling solution:



9.2 The hydrogen ion concentration of the internal solution is measured by the pH electrode located behind the membrane. Since the hydrogen ion concentration is directly related to CO<sub>2</sub> concentration, the electrode response is Nernstian.

9.3 Samples are treated prior to measurement with a buffer solution that sets the pH between 4.8 and 5.2. At this pH, interferences are minimized and the various ionic forms are converted to CO<sub>2</sub> (see Section 10).

## 10. Interferences

10.1 Volatile weak acids are potential positive electrode interferences. Concentrations of these interfering species that cause a 10 % error at 44 mg/L CO<sub>2</sub> or 100 mg/L (as CaCO<sub>3</sub>) and at pH 4 and 5, are listed below:

Interferences, mg/L	pH 5	pH 4
H <sub>2</sub> S	10	7
NO <sub>2</sub> <sup>-</sup> (NO <sub>2</sub> )	161	24
HSO <sub>3</sub> <sup>-</sup> (SO <sub>2</sub> )	320 (as SO <sub>2</sub> )	48 (as SO <sub>2</sub> )
HOAc (acetic acid)	372	216
HCOOH (formic acid)	1841	345

10.2 Samples containing sulfide can be treated with dilute solutions of potassium dichromate (or the like), since sulfur is not an interference for this test method. However, it is possible that some organic material could be oxidized to CO<sub>2</sub> by this treatment, resulting in falsely high results. The suitability of the test method for samples containing sulfide should be determined individually.

10.3 Water vapor is a potential electrode interference. Water can move across the membrane as water vapor, changing the concentration of the internal filling solution under the membrane. Such changes will be seen as electrode drift. Water vapor transport is not a problem if (1) the total concentration of dissolved species in solution (**Note 1**) is approximately equal to that of the internal filling solution, and (2) electrode and sample temperatures are the same.

**NOTE 1**—The osmotic strength of a solution is related to the total concentration of dissolved species in the solution. For example, the osmotic strength of a solution containing 0.1 M hydrochloric acid, 0.1 M acetic acid, and 0.1 M sucrose is determined as follows: Hydrochloric acid dissociates to give 0.1 M hydrogen ion and 0.1 M chloride ion. The acetic acid, because of the concentration of free hydrogen ion, is essentially undissociated; thus giving 0.1 M of species. Likewise, the concentration of sucrose species is 0.1 M. Therefore, the total osmotic strength is 0.4 osmolar.

10.4 Addition of carbon dioxide buffer (12.1) to samples of low osmotic strength automatically adjusts them to the correct level. Samples with osmotic strength greater than approximately 1 M should be diluted before measurement to avoid drifting associated with water vapor transport. Dilution should not reduce the carbon dioxide level below 2.5 mg/L. Samples with osmotic strengths above 1 M that cannot be diluted can be measured by adjusting the osmotic strength of the internal filling solution. To adjust the total concentration of dissolved species in the internal filling solution, add 0.425 g of reagent-grade NaNO<sub>3</sub> to 10 mL of internal filling solution.

## 11. Apparatus

- 11.1 *pH Meter*, with expanded mV scale, or a selective ion meter.
- 11.2 *CO<sub>2</sub> Gas-Sensing Electrode*.<sup>4</sup>
- 11.3 *Mixer*, magnetic with TFE-fluorocarbon-coated stirring bar or equivalent.

## 12. Reagents and Materials

12.1 *Buffer Solution*—Dissolve 294 g of sodium citrate in approximately 700 mL of water in a 1-L volumetric flask. Acidify the solution to pH 4.5 with concentrated HCl (approximately 90 mL) and dilute to the mark with water.

12.2 *Sodium Bicarbonate Solution, Standard (0.1 M)*—Dissolve 8.40 g of sodium bicarbonate in water and dilute to 1 L.

12.3 *Sodium Bicarbonate Solution, Standard (0.01 M)*—  
Dilute 10.0 mL of sodium bicarbonate standard solution (0.1 M) to 100 mL.

12.4 *Filter Paper*—Purchase suitable filter paper. Typically the filter papers have a pore size of 0.45-μm membrane. Material such as fine-textured, acid-washed, ashless paper, or glass fiber paper are acceptable. The user must first ascertain that the filter paper is of sufficient purity to use without adversely affecting the bias and precision of the test method.

<sup>4</sup> There are currently several manufacturers of the gas-sensing electrodes for carbon dioxide.

**13. Calibration and Standardization**

- 13.1 Assemble and check the electrode in accordance with the manufacturer’s instructions.
- 13.2 Dilute 10 mL of the buffer solution to 100 mL with water using a volumetric flask. Transfer the contents of the flask to a 150-mL beaker and add a stirring bar. Immerse the electrode in the solution. Stir at a slow rate using the magnetic stirrer.
- 13.3 Using a volumetric pipette, add 0.5 mL of the 0.01 M NaHCO<sub>3</sub> standard solution and mix slowly. Allow the potential reading to stabilize (approximately 10 min) and record the potential (corresponds to 2.2 mg/L CO<sub>2</sub> or 5.0 mg/L (as CaCO<sub>3</sub>)).
- 13.4 Using a volumetric pipette, add 0.5 mL of the 0.01 M NaHCO<sub>3</sub> standard solution and mix slowly. Allow the potential reading to stabilize (approximately 5 min) and record the potential (corresponds to 4.4 mg/L CO<sub>2</sub> or 10.0 mg/L (as CaCO<sub>3</sub>)).
- 13.5 Using a volumetric pipette, add 0.9 mL of the 0.1 M NaHCO<sub>3</sub> standard solution and mix slowly. Allow the potential reading to stabilize (approximately 2 min) and record the potential (corresponds to 43.2 mg/L CO<sub>2</sub> or 98.1 mg/L (as CaCO<sub>3</sub>)).
- 13.6 Using a volumetric pipette, add 10 mL of the 0.1 M NaHCO<sub>3</sub> standard solution and mix slowly. Allow the potential reading to stabilize (approximately 2 min) and record the potential (corresponds to 433 mg/L CO<sub>2</sub> or 983 mg/L (as CaCO<sub>3</sub>)).
- 13.7 ~~Plot~~ Follow manufacturer instructions for calibrating selective-ion meters with a direct reading of concentration capabilities. For pH meters, generate a calibration curve by creating a calibration curve by plotting potential values (on the linear scale) versus concentration (on the logarithmic scale) on semilogarithmic graph paper to obtain a calibration curve. The curve may be extended down to 2 mg/L and up to 800 mg/L CO<sub>2</sub>. Commercially available meters may be used.

**14. Procedure**

- 14.1 Bring samples to the same temperature as the electrode and standards.
- 14.2 Place a known volume, V<sub>s</sub>, (100 mL is convenient) of sample in 150-mL beaker and stir slowly. Immerse the electrode in the solution.
- 14.3 Add 1 mL of buffer, V<sub>b</sub>, for each 10 mL of sample. Allow the potential reading to stabilize and record the value. Read the concentration measured, C<sub>m</sub>, directly from the calibration curve.
- 14.4 Determine the sample concentration, C<sub>s</sub>, as follows:

$$C_s = C_m \frac{V_s + V_b}{V_s}$$

**15. Precision and Bias<sup>5</sup>**

15.1 *Precision*—The overall and single operator precision of this test method, within its designated range, varies with the quantity tested as shown in Fig. 1 for reagent water and Fig. 2 for selected water matrices. These matrices included natural waters

<https://standards.iteh.ai/catalog/standards/sist/d82c1a40-bb9c-4029-b885-6e7076660e9/astm-d513-16>

<sup>5</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:XXX-XXX RR:D19-1069. Contact ASTM Customer Service at service@astm.org.

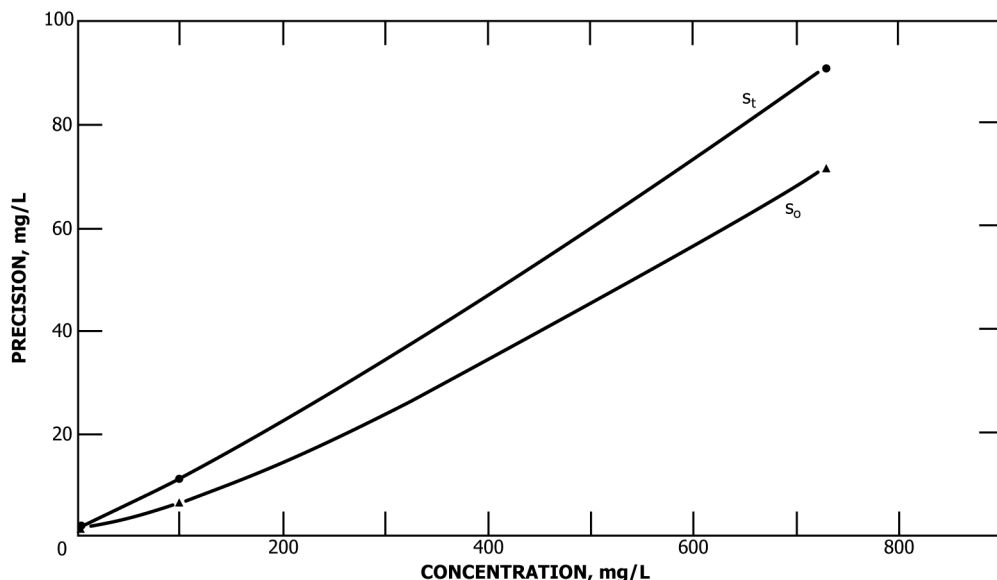


FIG. 1 Interlaboratory Precision for Total CO<sub>2</sub> Found in Reagent Water—Test Method A

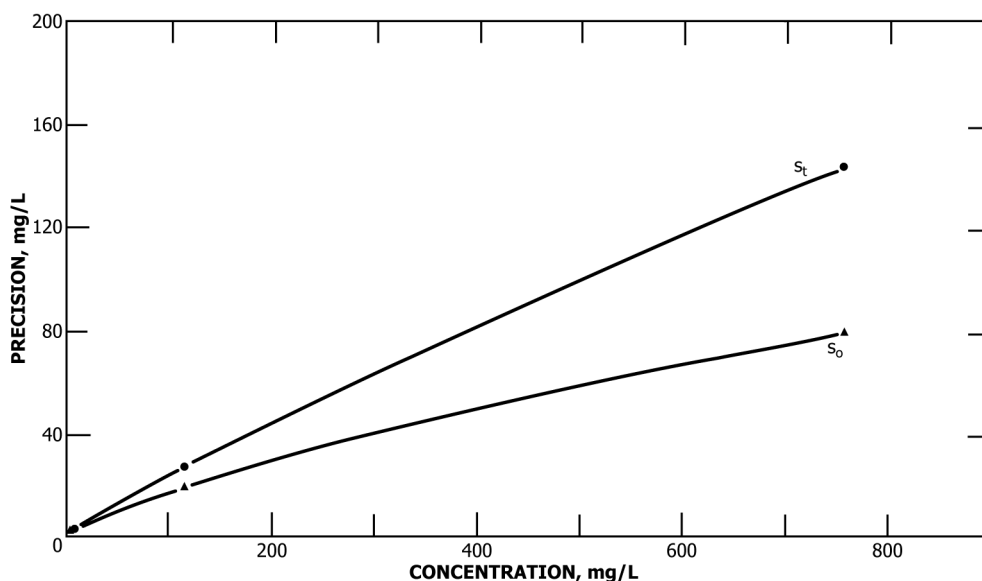


FIG. 2 Interlaboratory Precision for Total CO<sub>2</sub> Found in Selected Water Matrices—Test Method A

and brines.

15.2 *Bias*—Recoveries of known amounts of total CO<sub>2</sub> from reagent water and selected water matrices were as shown in Table 1.

15.3 The information in 15.1 and 15.2 is derived from round-robin testing in which eight laboratories, including twelve independent operators, participated. Of twelve data sets ranked as described in Practice D2777, four were rejected in the case of reagent water and three were rejected in the case of selected water matrices. Four outlier data points were also rejected. Four sample levels were run on three days, and blanks were obtained for the waters used.

15.4 Precision and bias for this test method conforms to Practice D2777 – 77, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of Practice D2777 – 08;13, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

**TEST METHOD B—CO<sub>2</sub> EVOLUTION, EVOLUTION, COULOMETRIC TITRATION TEST METHOD**

**16. Scope**

16.1 This test method determines total or dissolved carbon dioxide present as carbon dioxide, carbonic acid, bicarbonate ion, and carbonate ion in water within the interference constraints specified.

16.2 Carbon dioxide will also be detected from carbonates present in particulates in samples.

16.3 Samples containing between 5 and 800 mg/L total CO<sub>2</sub> can be analyzed by this test method. The concentration range may be extended upward by use of smaller samples or dilution of an appropriate aliquot. The range may be extended lower by use of larger samples.

TABLE 1 Bias—Test Method A

Amount Added, mg/L	Amount Found, mg/L	± %Bias	Statistically Significant (91 % Confidence Level)
<b>Reagent water</b>			
Reagent water			
2.1	2.7	+ 28.6	no
5.1	6.9	+ 35.3	yes
101	100	-1.0	no
803	730	-9.1	yes
<b>Water matrices</b>			
Water matrices			
2.1	3.0	+ 42.8	no
5.1	7.1	+ 39.2	yes
101	114	+ 12.9	no
803	754	-6.1	no

16.4 The precision and bias information reported in this test method was obtained in collaborative testing that included waters of the following types: distilled, deionized, potable, natural, brine, industrial waste, and waters derived from oil shale retorting. Since the precision and bias information reported may not apply to waters of all matrices, it is the user's responsibility to ensure the validity of the test method on samples of other matrices.

## 17. Summary of Test Method

17.1 Carbon dioxide is liberated by acidifying and heating the samples. The liberated CO<sub>2</sub> is swept through a scrubber by carbon dioxide-free air into an absorption cell where it is automatically coulometrically titrated. Concentrations of the several carbonate species are determined from the pH and total CO<sub>2</sub> values.

## 18. Interferences

18.1 Any volatile acid or base not removed by the scrubbing solution will interfere with the test. Potentially interfering gases that the scrubber removes include: hydrogen sulfide (H<sub>2</sub>S), chlorine (Cl<sub>2</sub>), bromine (Br<sub>2</sub>), hydrogen chloride (HCl), hydrogen bromide (HBr), hydrogen iodide (HI), hydrogen fluoride (HF), sulfur dioxide (SO<sub>2</sub>), and sulfur trioxide (SO<sub>3</sub>).

18.2 If a significant precipitate forms in the scrubber solution during an analysis, the scrubber solution should be replaced and the analysis repeated.

18.3 If the level of potentially interfering materials is such that the scrubber capacity is exhausted rapidly, an additional higher capacity scrubber may be added as directed in section 19.3. When two scrubbers are used, the scrubber capacity is considered to be exhausted when a precipitate begins forming in the final scrubber.

18.4 When analyzing samples that may evolve acid gases other than those listed, previously spiked samples should be analyzed to confirm that the scrubbers used are effective and, scrubbers should be modified if necessary.

## 19. Apparatus

19.1 *Carbon Dioxide Coulometer* to automatically titrate evolved carbon dioxide.<sup>6</sup>

19.2 *Carbon Dioxide Evolution Apparatus*, consisting of an air pump, air purification scrubber, acid dispenser, sample reaction chamber, and scrubber. The arrangement of the apparatus is shown in Fig. 3.

19.3 *High Capacity Scrubber*, if needed, may be assembled as illustrated in Fig. 4. It should be installed so the gas flows from the sample air outlet through the scrubber into the regular scrubber. The size may be increased over that specified, but doing so may lengthen the analysis time.

19.4 *pH Meter*, conforming to the requirements given in Test Methods D1293.

## 20. Reagents and Materials

20.1 *Coulometer Cell Reagents*—Cell solutions to absorb CO<sub>2</sub> from the gas stream and convert it to a titratable acid and permit 100 % efficient coulometric titration.

20.2 *Perchloric Acid Solution* (approximately 1 + 5)—Add 170 mL of concentrated HClO<sub>4</sub> (sp gr 1.67) to 500 mL of water, mix, and dilute to 1 L with water.

20.3 *Scrubber Solution*—Add 2 mL of concentrated HClO<sub>4</sub> (sp gr 1.67) and 5 g of silver perchlorate (AgClO<sub>4</sub>) to 100 mL of water. When adding scrubber solution to the scrubbers, and 0.1 mL of 30 % hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) to the scrubber per mL of scrubber solution used in the scrubber. As an alternative scrubber solution, use 2 mL of concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) per 100 mL of water saturated with silver sulfate (Ag<sub>2</sub>SO<sub>4</sub>) and add 30 % H<sub>2</sub>O<sub>2</sub> as for the AgClO<sub>4</sub> scrubber solution.

## 21. Calibration and Standardization

21.1 Calibration is not required; however, standards should be analyzed before analyzing samples and periodically to confirm proper operation of the instrument. If the recovery of a standard is unacceptable, the cause of the poor result should be determined and corrected. Generally low results are due to leaks, and high results are due to contamination of reagents or an exhausted scrubbers.

## 22. Procedure

22.1 *Blank Determination:*

22.1.1 Set up the CO<sub>2</sub> coulometer as directed by the instrument manufacturer.

<sup>6</sup> The sole source of supply of the apparatus known to the committee at this time is Coulometrics, Inc., a subsidiary of UIC Inc., P.O. Box 863, Joliet, IL 60434. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,<sup>1</sup> which you may attend.