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AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Test Methods for Total and Dissolved Carbon Dioxide in Water¹

This standard is issued under the fixed designation D 513; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 These test methods provide for the measurement of total or dissolved carbon dioxide present as carbon dioxide (CO₂), 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 ₂ 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 *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:

- D 1066 Practice for Sampling Steam²
- D 1129 Terminology Relating to Water²
- D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits²
- D 1193 Specification for Reagent Water²
- D 1293 Test Methods for pH of Water²
- D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water²
- D 3370 Practices for Sampling Water from Closed Conduits²
- E 200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis³

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3. Terminology

3.1 *Definitions*—For definitions of terms used in these test methods, refer to Terminology D 1129.

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 CO₂. 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, CO₂ contributes significantly to corrosion of water-handling systems. This is particularly troublesome in steam condensate systems. Loss of CO₂ 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 CO₂ 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.⁴ 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 D 1193. Additionally, for those test methods requiring water free of CO₂, refer to 8.2 of Practice E 200.

¹ These test methods are under the jurisdiction of ASTM Committee D-19 on Water and are the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

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² *Annual Book of ASTM Standards*, Vol 11.01.

³ *Annual Book of ASTM Standards*, Vol 15.05.

⁴ *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.

6. Precautions

6.1 **Caution**—Carbon dioxide is easily lost from solution during transit and storage of samples. It is also possible for total CO₂ 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 D 1066 and D 3370 and Specification D 1192, 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 CO₂ 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 TEST METHOD

8. Scope

8.1 This test method determines total or dissolved carbon dioxide (9.2) present as CO₂, carbonic acid, bicarbonate ion, and carbonate ion in water, within the interference constraints specified.

8.2 Samples containing 2 to 800 mg/L total CO₂ can be analyzed by this test method. The concentration range may be extended by dilution of an appropriate aliquot.

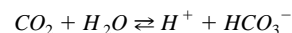
8.3 Samples should be analyzed immediately. If this is not possible, preserve by making them slightly alkaline (pH between 8 and 9) using carbonate-free NaOH solution and store them in a tightly capped vessel. The latter step prevents absorption of CO₂ from the air.

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.

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 CO₂ in the sample solution and the CO₂ in the internal filling solution. In any given sample, the partial pressure of CO₂ will be propor-

tional to the concentration of CO₂. The diffusion of CO₂ across the membrane affects the concentration of hydrogen ions in the internal filling solution:



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 CO₂ concentration, the electrode response is Nernstian.

9.2 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 CO₂ (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 CO₂ or 100 mg/L (as CaCO₃) and at pH 4 and 5, are listed below:

Interferences, mg/L	pH 5	pH 4
H ₂ S	10	7
NO ₂ ⁻ (NO ₂)	161	24
HSO ₃ ⁻ (SO ₂)	320 (as SO ₂)	48 (as SO ₂)
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 CO₂ 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 NaNO₃ to 10 mL of internal filling solution.

11. Apparatus

11.1 *pH Meter*, with expanded mV scale, or a selective ion meter.

11.2 *CO₂ Gas-Sensing Electrode*⁵.

11.3 *Mixer*, magnetic with TFE-fluorocarbon-coated stirring bar or equivalent.

12. Reagents

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.

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 pipet, add 0.5 mL of the 0.01 M NaHCO₃ standard solution and mix slowly. Allow the potential reading to stabilize (approximately 10 min) and record the potential (corresponds to 2.2 mg/L CO₂ or 5.0 mg/L (as CaCO₃)).

13.4 Using a volumetric pipet, add 0.5 mL of the 0.01 M NaHCO₃ standard solution and mix slowly. Allow the potential reading to stabilize (approximately 5 min) and record the potential (corresponds to 4.4 mg/L CO₂ or 10.0 mg/L (as CaCO₃)).

13.5 Using a volumetric pipet, add 0.9 mL of the 0.1 M NaHCO₃ standard solution and mix slowly. Allow the potential reading to stabilize (approximately 2 min) and record the potential (corresponds to 43.2 mg/L CO₂ or 98.1 mg/L (as CaCO₃)).

13.6 Using a volumetric pipet, add 10 mL of the 0.1 M NaHCO₃ standard solution and mix slowly. Allow the potential reading to stabilize (approximately 2 min) and record the potential (corresponds to 433 mg/L CO₂ or 983 mg/L (as CaCO₃)).

13.7 Plot 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 CO₂.

⁵ The sole source of supply of the apparatus known to the committee at this time is Orion Research Inc., 529 Main St., Boston, MA 02129. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend.

14. Procedure

14.1 Bring samples to the same temperature as the electrode and standards.

14.2 Place a known volume, V_s , (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_b , for each 10 mL of sample. Allow the potential reading to stabilize and record the value. Read the concentration measured, C_m , directly from the calibration curve.

14.4 Determine the sample concentration, C_s , as follows:

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

15. Precision and Bias ⁶

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 and brines.

15.2 *Bias*—Recoveries of known amounts of total CO₂ 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 D 2777, 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.

TEST METHOD B—CO₂ 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 CO₂ 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.

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.

⁶ Supporting data for this test method are available from ASTM Headquarters. Request RR:D19-1069.

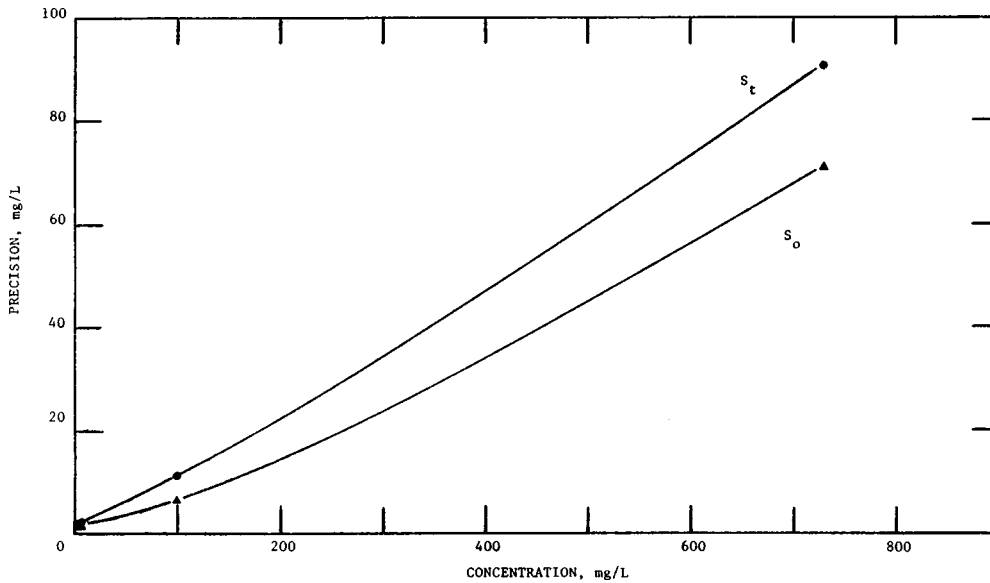


FIG. 1 Interlaboratory Precision for Total CO₂ Found in Reagent Water—Test Method A

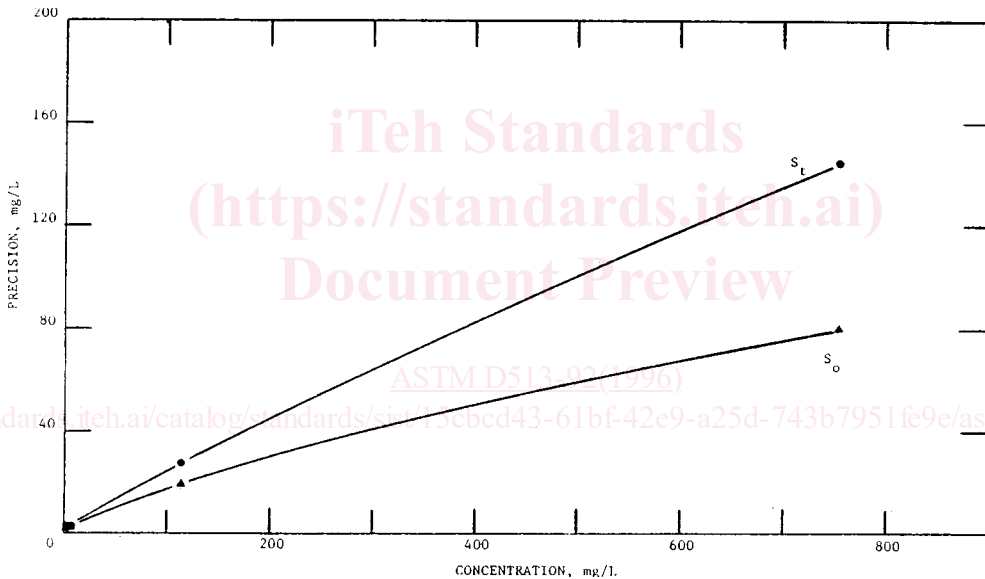


FIG. 2 Interlaboratory Precision for Total CO₂ Found in Selected Water Matrices—Test Method A

TABLE 1 Bias—Test Method A

Amount Added, mg/L	Amount Found, mg/L	± %Bias	Statistically Significant (91 % Confidence Level)
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
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

17. Summary of Test Method

17.1 Carbon dioxide is liberated by acidifying and heating the samples. The liberated CO₂ 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 CO₂ 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 (H₂S), chlorine (Cl₂), bromine (Br₂), hydrogen chloride (HCl), hydrogen bromide (HBr), hydrogen iodide (HI), hydrogen fluoride (HF), sulfur dioxide (SO₂), and sulfur trioxide (SO₃).

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 under 19.3.