



Standard Test Method for Total Carbon and Organic Carbon in Water by Ultraviolet, or Persulfate Oxidation, or Both, and Infrared Detection¹

This standard is issued under the fixed designation D4839; 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 This test method covers the determination of total carbon (TC), inorganic carbon (IC), and total organic carbon (TOC) in water, wastewater, and seawater in the range from 0.1 mg/L to 4000 mg/L of carbon.

1.2 This test method was used successfully with reagent water spiked with sodium carbonate, acetic acid, and pyridine. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

1.3 This test method is applicable only to carbonaceous matter in the sample that can be introduced into the reaction zone. The syringe needle or injector opening size generally limit the maximum size of particles that can be so introduced.

1.4 In addition to laboratory analyses, this test method may be applied to stream monitoring.

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

1.6 *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:*²

[D1129 Terminology Relating to Water](#)

[D1192 Guide for Equipment for Sampling Water and Steam in Closed Conduits](#) (Withdrawn 2003)³

¹ This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.06 on Methods for Analysis for Organic Substances in Water.

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

³ The last approved version of this historical standard is referenced on www.astm.org.

[D1193 Specification for Reagent 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](#)

[D4129 Test Method for Total and Organic Carbon in Water by High Temperature Oxidation and by Coulometric Detection](#)

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

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology [D1129](#).

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *inorganic carbon (IC)*—carbon in the form of carbon dioxide, carbonate ion, or bicarbonate ion.

3.2.2 *total organic carbon (TOC)*—carbon in the form of organic compounds.

3.2.3 *total carbon (TC)*—the sum of IC and TOC.

3.2.4 *refractory material*—that which cannot be oxidized completely under the test method conditions.

4. Summary of Test Method

4.1 *Fundamentals*—Carbon can occur in water as an inorganic and organic compound. This test method can be used to make independent measurements of IC, TOC, and TC, and can also determine IC by the difference of TC and TOC, and TOC as the difference of TC and IC.

4.2 The essentials of this test method are: (a) removal of IC, if desired, by acidification of the sample and sparging by carbon-free gas; (b) conversion of remaining carbon to CO₂ by action of persulfate, aided either by elevated temperature or ultraviolet (UV) radiation; (c) detection of CO₂ that is swept out of the reactor by a gas stream; and (d) conversion of detector signal to a display of carbon concentration in mg/L. A diagram of suitable apparatus is given in [Fig. 1](#).

5. Significance and Use

5.1 This test method is used for determination of the carbon content of water from a variety of natural, domestic, and industrial sources. In its most common form, this test method

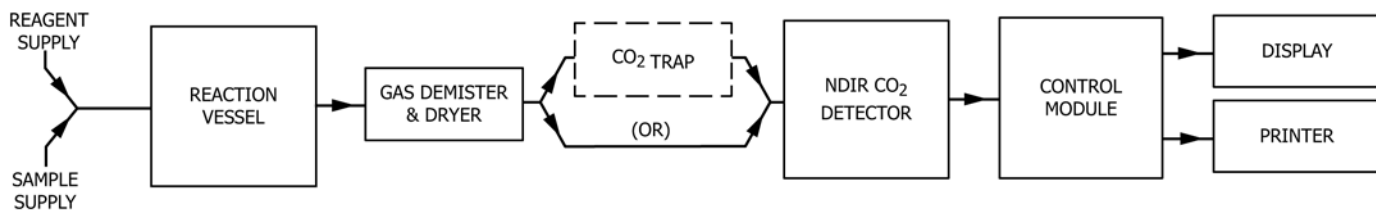


FIG. 1 Diagram of Apparatus

is used to measure organic carbon as a means of monitoring organic pollutants in industrial wastewater. These measurements are also used in monitoring waste treatment processes.

5.2 The relationship of TOC to other water quality parameters such as chemical oxygen demand (COD) and total oxygen demand (TOD) is described in the literature.⁴

6. Interferences and Limitations

6.1 The oxidation of dissolved carbon to CO₂ is brought about at relatively low temperatures by the chemical action of reactive species produced by hot or UV-irradiated persulfate ions. Even if oxygen is used as the sparging gas, it makes a much lower contribution to oxidation than in high-temperature (combustive) systems. Not all suspended or refractory material may be oxidized under these conditions; analysts should take steps to determine what recovery is being obtained. This may be done by several methods: (a) by monitoring reaction progress to verify that oxidation has been completed; (b) by rerunning the sample under more vigorous reaction conditions; (c) by analyzing the sample by an alternative method, such as Test Method D4129, known to result in full recovery; or (d) by spiking samples with known refractories and determining recovery.

6.2 Chloride ion tends to interfere with oxidative reaction mechanisms in this test method, prolonging oxidation times and sometimes preventing full recovery. Follow manufacturer's instructions for dealing with this problem. See Appendix X1 for supporting data.

6.3 Homogenizing or sparging of a sample, or both, may cause loss of purgeable organic compounds, thus yielding a value lower than the true TOC level. (For this reason, such measurements are sometimes known as nonpurgeable organic carbon (NPOC)). The extent and significance of such losses must be evaluated on an individual basis. This may be done by comparing the TOC by difference (TC-IC) with the direct TOC figure, that is, that obtained from a sparged sample. The difference, if any, between these TOC figures represents purgeable organic carbon (POC) lost during sparging. Alternatively, direct measurement of POC can be made during sparging, using optional capabilities of the analyzer.

6.4 Note that error will be introduced when the method of difference is used to derive a relatively small level from two large levels. For example, a ground water high in IC and low in TOC will give a poorer TOC value as (TC-IC) than by direct measurement.

7. Apparatus

7.1 *Homogenizing Apparatus*—A household blender is generally satisfactory for homogenizing immiscible phases in water.

7.2 *Sampling Devices*—Microlitre-to-millilitre syringes are typically required for this test method. Alternatives include manually operated or automatically operated sampling valves. Sampling devices with inside diameters as small as 0.15 mm may be used with samples containing little or no particulate matter. Larger inside dimensions such as 0.4 mm will be required for samples with particulate matter.

NOTE 1—See 6.1 concerning oxidation of particulate matter.

7.3 *Apparatus for Carbon Determination*—This instrument consists of reagent and sample introduction mechanism, a gas-sparged reaction vessel, a gas demister or dryer, or both, an optional CO₂ trap, a CO₂-specific infrared detector, a control system, and a display. Fig. 1 shows a diagram of such an arrangement.

7.3.1 Sparging requires an inert vessel with a capacity of at least double the sample size with provision for sparging with 50 to 100 mL/min of carbon free gas. This procedure will remove essentially all IC in 2 to 10 min, depending on design.

7.3.2 *Oxidation*—The reaction assembly contains reagent and sample introduction devices, and a reactor vessel with sparging flow of carbon-free gas. The vessel may be heated by an external source, and may contain a UV lamp. The reaction vessel and sparging vessel (see 6.3) may be combined.

7.3.3 *Gas Conditioning*—The gas passing from the reactor is dried, and the CO₂ produced is either trapped and later released to the detector, or routed directly to the detector through a chlorine-removing scrubber.

7.3.4 *Detector*—The CO₂ in the gas stream is detected by a CO₂-specific nondispersive infrared (NDIR) detector.

7.3.5 *Presentation of Results*—The NDIR detector output is related to stored calibration data and then displayed as milligrams of carbon per litre.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on

⁴ Handbook for Monitoring Industrial Wastewater, Section 5.3, U.S. Environment Protection Agency, August 1973, pp. 5–12.

Analytical Reagents of the American Chemical Society,⁵ where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficient purity to permit its use without lessening the accuracy of the determination.

8.2 Purity of Water—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification **D1193**, Type I or Type II. The indicated specification does not actually specify inorganic carbon or organic carbon levels. These levels can affect the results of this test method, especially at progressively lower levels of the carbon content in the samples to be measured. Where inorganic carbon in reagent water is significant, CO₂-free water may be prepared from reagent water by acidifying to pH 2, then sparging with fritted-glass sparger using CO₂-free gas (time will depend on volume and gas flow rate, and should be determined by test). Alternatively, if the carbon contribution of the reagent water is known accurately, its effect may be allowed for in preparation of standards and other solutions. CO₂-free water should be protected from atmospheric contamination. Glass containers are required for storage of water and standard solutions.

8.3 Acid—Various concentrated acids may be used for acidification of samples and of the oxidizing reagent. Acids such as phosphoric (sp gr 1.69), nitric (sp gr 1.42), or sulfuric (sp gr 1.84) are suitable for most applications. Sulfuric acid should be used in the form of a 1 + 1 dilution, for safety reasons. Hydrochloric acid is not recommended.

8.4 Organic Carbon, Standard Solution (2000 mg/L)—Choose a water-soluble, stable reagent grade compound, such as benzoic acid or anhydrous potassium hydrogen phthalate (KHC₈H₄O₄). Calculate the weight of compound required to make 1 L of organic carbon standard solution; for example, KHC₈H₄O₄ = 0.471 g of carbon per gram, so one litre of 2 g/L of standard requires 2/0.471, or 4.25, grams of KHP. Dissolve the required amount of standard in some CO₂-free water in a 1-L volumetric flask, add 1 mL of acid, and dilute to volume. This stock solution, or dilutions of it, may be used to calibrate and test performance of the carbon analyzer.

8.5 Persulfate Solution—Prepare by dissolving the appropriate weight of potassium or sodium persulfate in 1 L of water, to produce the concentration specified by the instrument manufacturer. If specified, add 1 mL of phosphoric acid (sp gr 1.69) and mix well. Store in a cool, dark place. Recipes for this reagent solution may be modified by manufacturers to meet the needs of specific applications, for example, high chloride samples.

8.6 Gas Supply—A gas free of CO₂ and of organic matter is required. Use a purity as specified by the equipment manufacturer. The use of oxygen is preferred for the UV-persulfate

method, and nitrogen or helium is preferred if a CO₂ trap is used between reactor and detector.

9. Sampling and Sample Preservation

9.1 Collect the sample in accordance with Specification **D1192** and Practice **D3370**.

9.2 To preserve samples for this analysis, store samples in glass at 4°C. To aid preservation, acidify the samples to a pH of 2. It should be noted that acidification will enhance loss of inorganic carbon. If the purgeable organic fraction is important, fill the sample bottles to overflowing with a minimum of turbulence and cap them using a fluoropolymer-lined cap, without headspace.

9.3 For monitoring of waters containing solids or immiscible liquids that are to be injected into the reaction zone, use a mechanical homogenizer or ultrasonic disintegrator. Filtering or screening may be necessary after homogenization to reject particle sizes that are too large for injection. Volatile organics may be lost. See **6.3**.

9.4 For wastewater streams where carbon concentrations are greater than the desired range of instrument operation, dilute the samples as necessary.

10. Instrument Operation

10.1 Follow the manufacturer's instructions for instrument warm-up, gas flows, and liquid flows.

11. Calibration

11.1 Use the stock solution of 2000 mg/L of carbon, and various dilutions of it, for calibration.

NOTE 2—Dilutions should be made with CO₂-free water (see **8.2**).

11.2 Calibration protocols may vary with equipment manufacturers. However, in general, calibrate the instrument in accordance with the manufacturer's instructions, and use standards to verify such calibration in the specific range of interest for actual measurements. Plots of standard concentration versus instrument reading may be used for calibration or to verify linearity of response.

11.3 Establish instrument blank according to the manufacturer's instructions.

12. Procedure

12.1 Mix or blend each sample thoroughly and carry out any necessary dilution to bring the carbon content within range of the instrument.

12.2 If inorganic carbon is to be measured directly, inject the sample into the analyzer under appropriate conditions.

12.3 If inorganic carbon is to be removed by sparging prior to sample introduction, acidify to approximately pH 2 with concentrated acid (if not already done) and sparge with an appropriate flow of gas. Samples with high alkali content or buffer capacity may require larger amounts of acid. In such cases, incorporate this dilution into the calculation. If incomplete sparging of CO₂ from IC is suspected, sparge and analyze the sample and then repeat the procedure until appropriate

⁵ *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.

conditions are established. In difficult conditions, use of a fritted-glass sparger may help.

12.4 To measure TOC, inject an appropriate volume of the sample into the analyzer. If external sparging is required to remove IC, inject a sparged sample for the TOC measurement. See 6.3.

12.5 To measure TC, inject an appropriate volume of unsparged sample.

13. Calculation

13.1 Read carbon values directly from a digital display or printer, or both.

14. Precision and Bias⁶

14.1 Collaborative Test—This test method was evaluated by sending seven identical samples to each of ten laboratories and asking them to measure TOC and TC exactly in accordance with this test method. Three of the ten laboratories did not make the TC measurement. One of the samples consisted of laboratory reagent water. The other six were of that water spiked to various levels with acetic acid, pyridine, and sodium carbonate. TC levels ranged from 0.6 to 2 000 mg/L, and TOC levels from 0.3 to 1 700 mg/L. An *F* test at 95 % confidence level showed no significant difference between the results of the five laboratories using UV-persulfate oxidation and those of the five laboratories using hot persulfate. Consequently, results were pooled for further analysis.

14.2 Removal of Outliers—Application of outlier tests specified in Practice D2777 – 85 resulted in the elimination of one laboratory’s TC and TOC results. In addition, three laboratories did not perform the TC analysis, so the effective number of laboratories was six for the TC measurement. Five of their individual results were later eliminated by outlier test. In the TOC determination, one additional laboratory failed the outlier test, leaving a total of eight. Three individual results were later eliminated.

14.3 Precision—Separate determinations of precision were made for TC and TOC measurements:

For TC: $S_t = 0.03x + 0.3$

$S_o = 0.01x + 0.2$

For TOC: $S_t = 0.08x + 0.1$

$S_o = 0.04x + 0.1$

where:

x = the recovered *C* concentration, mg/L,

S_t = overall precision, and

S_o = single-operator precision.

Fig. 2 shows a log-log plot of the overall and single-operator precision of all TC and TOC measurements not eliminated by outlier tests.

14.4 Bias—Fig. 3 plots “amount added” against “amount found,” with overall precision shown as an error bar. Bias

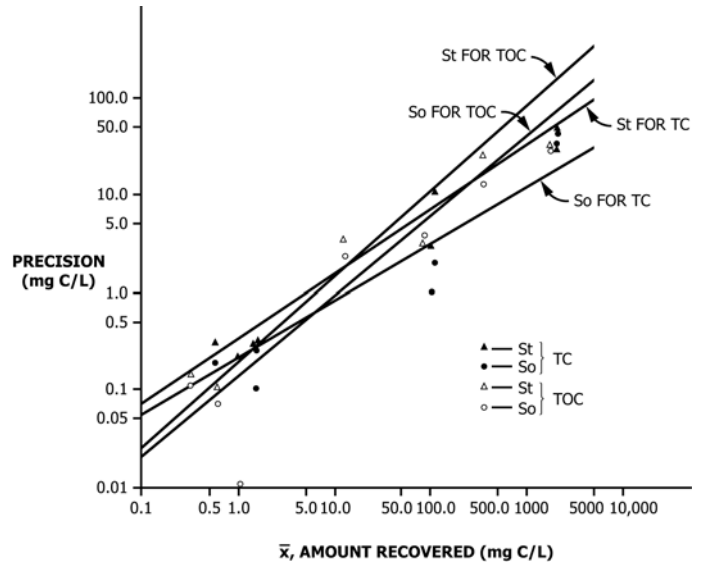


FIG. 2 Precision Versus Amount Recovered

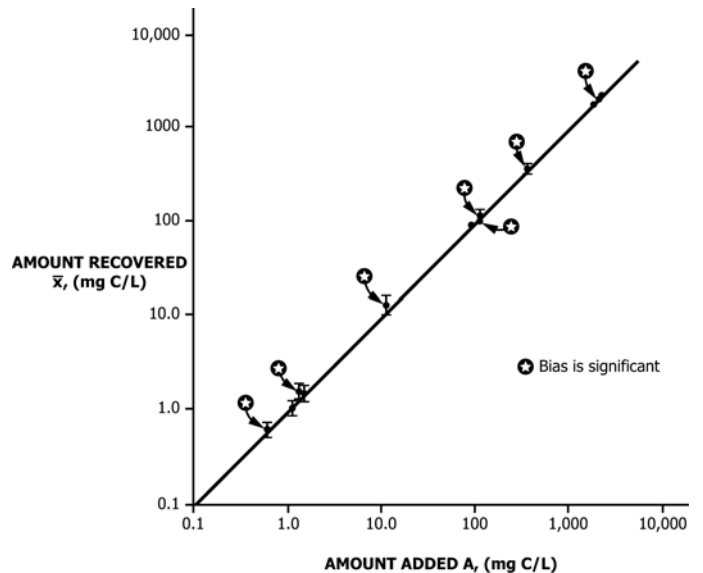


FIG. 3 Bias: Amount Added Versus Amount Recovered

significant at the 95 % level (student’s *t*-test) is flagged. Water that was used as one of the samples is omitted, since no value equivalent to “amount added” is available. The contribution of the carbon in the water to the spiked samples was allowed for before analysis of bias. In general, bias is positive, with the values running from 1 % to 25 % of the amount added, with no particular pattern evident. Of the twelve bias measurements, ten were below 10 %. Users of this test method should make their own determination of bias.

14.5 Matrix Effects—Participants were asked to measure the TC and TOC levels in a water sample of their choice, and then to spike the sample with one of the study samples and to measure the sample again. The chosen samples were: sink waste; DI water with KHP; soil solution; tap water with added IC; plant waste stream; synthetic sewage, and anion resin brine wash. TC recoveries averaged 86 % (range from 74 % to 92 %), and TOC, 82 % (from 47 % to 92 %). The negative bias,

⁶ Supporting data are available from ASTM Headquarters. Request RR: D-19-1130.

versus the positive bias noted in 14.4, can reflect incomplete oxidation of spiking compounds in the presence of other organics, errors introduced by sample handling, or other effects. In any event, no one matrix was studied in sufficient depth to provide an answer. Users of this test method should conduct their own experiments to determine recovery in their particular circumstances.

15. Quality Assurance/Quality Control

15.1 In order to be certain that analytical values obtained using this test method are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when running the test.

15.2 *Calibration and Calibration Verification*—See 11.1.

15.3 *Analyst Performance Check*—If a laboratory has not performed the test before or if there has been a major change in the measurement system, for example, new analyst, new instrument, etc., a precision and bias study must be performed to demonstrate laboratory capability.

15.3.1 Analyze seven replicates of a standard solution prepared from a certified reference material containing a concentration of analyte similar to that expected in test samples and within the range of 0.1 to 4000 mg/L. Each replicate must be taken through the complete analytical test method including any sample preservation and pretreatment steps. The replicates may be interspersed with samples.

15.3.2 Calculate the mean and standard deviation of these values and compare to the acceptable ranges of precision and bias that may be calculated by the user using the precision and bias relationships listed in Section 14. This study should be repeated until the single operator precision and the mean recovery are within acceptable limits. If a concentration other than the recommended concentration is used, refer to Practice D5847 for information on applying the *F* test and *t* test in evaluating the acceptability of the mean and standard deviation.

15.4 *Laboratory Control Sample (LCS)*—To insure that the test method is in control, analyze an LCS at the beginning and ending of a sequence of samples. If large numbers of samples are analyzed in a single day, analyze the LCS after every 20 samples. The LCS must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The value obtained for the LCS should be within $\pm 3S_r$ control limits that may be calculated from the S_r and 0 relationships in 14. If the result is not within these limits, analysis of samples is halted until the problem is corrected, and either all samples in the Batch must be reanalyzed, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

15.5 *Method Blank*—Analyze a test method blank each time the test is run. Use low TOC reagent water in place of a sample and analyze as described in Section 12. The variability of blank values obtained must be less than that specified by the user after consideration of the precision and bias relationships near zero concentration.

15.6 *Matrix Spike (MS)*—To check for interferences in the specific matrix being tested, perform a MS on at least one sample from each set of samples being analyzed by spiking an aliquot of the sample with a known concentration of analyte and taking it through the complete analytical method.

15.6.1 The spike concentration plus the background concentration of the analyte must not exceed the upper limit of the method. The spike must produce a concentration in the spiked sample 2 to 5 times the background concentration or 10 to 50 times the detection limit of the test method, whichever is greater.

15.6.2 Calculate the percent recovery of the spike (*P*) using the following formula:

$$P = 100[A(V_s + V) - B V_s]/C V \quad (1)$$

where:

- A* = analyte concentration (mg/L) in spiked sample,
- B* = analyte concentration (mg/L) in unspiked sample,
- C* = concentration (mg/L) of analyte in spiking solution,
- V_s = volume (mL) of sample used, and
- V* = volume (mL) added with spike.

15.6.3 The percent recovery of the spike shall fall within limits to be specified in advance by the user. If the percent recovery is not within these limits, a matrix interference may be present in the sample selected for spiking. Under these circumstances, one of the following remedies must be employed: (1) the matrix interference must be removed, (2) all samples in the Batch must be analyzed by a test method not affected by the matrix interference, or (3) the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

15.7 *Duplicate*:

15.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each sequence of samples to be analyzed.

15.7.2 Calculate the standard deviation of the duplicate values and compare to the single operator precision in the collaborative study using an *F* test. Refer to 6.4.4 of Practice D5847 for information on applying the *F* test.

15.7.3 If the result exceeds the precision limit, the Batch must be reanalyzed or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

15.8 *Independent Reference Material (IRM)*—In order to verify the quantitative value produced by the test method, analyze an IRM submitted as a regular sample (if practical) to the laboratory at least once per quarter. The concentration of the reference material should be in the range of the test method. The value obtained must fall within the control limits specified by the outside source.

16. Keywords

16.1 carbon; carbon dioxide; low temperature oxidation; organic carbon; total carbon

APPENDIX
(Nonmandatory Information)
X1. RECOVERIES OF VARIOUS COMPOUNDS FROM CHLORIDE-CONTAINING SOLUTIONS WITH UV-PERSULFATE OXIDATION

X1.1 *Conditions*— Inject into the instrument 200 μ L of solution, containing 100 ppm of carbon in the form of the compound indicated plus 1.8 % of chloride ion. Take results at the completion of oxidation or after 8 min, whichever occurs first.

TABLE X1.1 Percent Recovery

Analyte	No Mercuric Reagent	With Mercuric Reagent
Potassium hydrogen phthalate	90.5	101.2
Urea	101.1	...
Methanol	96.6	99.3
Nicotinic acid	91.0	97.9
Pyridine	88.6	98.0
Proline	86.0	92.2
<i>n</i> -Butanol	74.3	96.2
Acetic acid	66.5	101.3
Leucine	64.7	96.6
Acetonitrile	5.0	88.0

TABLE X1.2 Recoveries of Potassium Hydrogen Phthalate from Chloride-Containing Solutions Using Hot Persulfate Oxidation

ppm of Carbon	Recovery
200	99.4 %
800	92.0 %

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