



# Standard Test Methods for Nickel in Water<sup>1</sup>

This standard is issued under the fixed designation D 1886; 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 approval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

*This standard has been approved for use by agencies of the Department of Defense.*

## 1. Scope\*

1.1 These test methods<sup>2, 3, 4</sup> cover the atomic absorption determination of nickel in water and wastewaters. Three test methods are given as follows:

	Concentration Range	Sections
Test Method A—Atomic Absorption, Direct	0.1 to 10 mg/L	7-16
Test Method B—Atomic Absorption, Chelation-Extraction	10 to 1000 $\mu$ g/L	17-26
Test Method C—Atomic Absorption, Graphite Furnace	5 to 100 $\mu$ g/L	27-36

1.2 Test Methods A, B, and C have been used successfully with reagent grade water and natural waters. Evaluation of Test Method C was also made in condensate from a medium Btu coal gasification process. It is the user's responsibility to ensure the validity of these test methods for other matrices.

1.3 *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 hazards statements, see Note 4, 11.7.1, 21.9, 23.7, and 23.10.

1.4 Two former colorimetric test methods were discontinued. Refer to Appendix X1 for historical information.

## 2. Referenced Documents

### 2.1 ASTM Standards:

- D 858 Test Methods for Manganese in Water<sup>5</sup>
- D 1066 Practice for Sampling Steam<sup>5</sup>

<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.

Current edition approved June 10, 2003. Published July 2003. Originally approved in 1961. Last previous edition approved in 1998 as D1886 – 94 (1998).

<sup>2</sup> Chilton, J. M., "Simultaneous Colorimetric Determination of Copper, Cobalt, and Nickel as Diethyldithiocarbamates," *Analytical Chemistry*, Vol 25, 1953, pp. 1274–1275.

<sup>3</sup> Platte, J. A., and Marcy, V. M., "A New Tool for the Water Chemist," *Industrial Water Engineering*, May 1965.

<sup>4</sup> Brown, E., Skougstad, M. W., and Fishman, M. J., "Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases," *Techniques of Water-Resources Investigations of the U.S. Geological Survey*, Book 5, Chapter , 1970, p. 115.

<sup>5</sup> *Annual Book of ASTM Standards*, Vol 11.01.

- D 1068 Test Methods for Iron in Water<sup>5</sup>
- D 1129 Terminology Relating to Water<sup>5</sup>
- D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits<sup>5</sup>
- D 1193 Specification for Reagent Water<sup>5</sup>
- D 1687 Test Methods for Chromium in Water<sup>5</sup>
- D 1688 Test Methods for Copper in Water<sup>5</sup>
- D 1691 Test Methods for Zinc in Water<sup>5</sup>
- D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water<sup>5</sup>
- D 3370 Practices for Sampling Water from Closed Conduits<sup>5</sup>
- D 3557 Test Methods for Cadmium in Water<sup>5</sup>
- D 3558 Test Methods for Cobalt in Water
- D 3559 Test Methods for Lead in Water<sup>5</sup>
- D 3919 Practice for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry<sup>5</sup>
- D 4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents<sup>5</sup>
- D 5810 Guide for Spiking into Aqueous Samples<sup>5</sup>
- D 5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis<sup>6</sup>

## 3. Terminology

### 3.1 Definitions:

3.1.1 For definitions of terms used in these test methods, refer to Terminology D 1129.

### 3.2 Definitions of Terms Specific to This Standard:

3.2.1 *total recoverable nickel*—an arbitrary analytical term relating to the recoverable forms of nickel that are determinable by the digestion method that is included in these test methods.

## 4. Significance and Use

4.1 Elemental constituents in potable water, receiving water, and wastewater need to be identified for support of effective pollution control programs. Test Methods A, B, and C provide the techniques necessary to make such measurements.

4.2 Nickel is considered to be relatively nontoxic to man and a limit for nickel is not included in the EPA National

<sup>6</sup> *Annual Book of ASTM Standards*, Vol 11.02.

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

Interim Primary Drinking Water Regulations.<sup>7</sup> The toxicity of nickel to aquatic life indicates tolerances that vary widely and that are influenced by species, pH, synergistic effects, and other factors.

4.3 Nickel is a silver-white metallic element seldom occurring in nature in the elemental form. Nickel salts are soluble and can occur as a leachate from nickel-bearing ores. Nickel salts are used in metal-plating and may be discharged to surface or ground waters.

## 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 where such specifications are available.<sup>8</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 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193, Type I. 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 lessening the bias and precision of the determination. Type II water was specified at the time of the round-robin testing of this test method.

## 6. Sampling

6.1 Collect the sample in accordance with Practice D 1066, Specification D 1192, or Practices D 3370, as applicable.

6.2 Samples shall be preserved with HNO<sub>3</sub> (sp gr 1.42) to a pH of 2 or less immediately at the time of collection, normally about 2 mL/L. If only dissolved nickel is to be determined, the sample shall be filtered through a 0.45- $\mu$ m membrane filter before acidification. The holding time for samples may be calculated in accordance with Practice D 4841.

## TEST METHOD A—ATOMIC ABSORPTION, DIRECT

### 7. Scope

7.1 This test method covers the determination of dissolved and total recoverable nickel and has been used successfully with reagent water, tap water, river water, lake water, ground water, a refinery effluent, and a wastewater.

7.2 This test method is applicable in the range from 0.1 to 10 mg/L of nickel. The range may be extended upward by dilution of the sample.

<sup>7</sup> EPA Publication No. EPA-570/9-76-003 was originally published in 1976, and amended in 1980. Contact the Environmental Protection Agency, 401 "M" ST., S.W., Washington, DC 20406 for availability.

<sup>8</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.

## 8. Summary of Test Method

8.1 Nickel is determined by atomic absorption spectrophotometry. Dissolved nickel is determined by aspirating the filtered sample directly with no pretreatment. Total recoverable nickel is determined by aspirating the sample following hydrochloric-nitric acid digestion and filtration. The same digestion procedure is used for cadmium (Test Methods D 3557), chromium (Test Methods D 1687), cobalt (Test Methods D 3558), copper (Test Methods D 1688), iron (Test Methods D 1068), lead (Test Methods D 3559), manganese (Test Methods D 858), and zinc (Test Methods D 1691).

## 9. Interferences

9.1 Sodium, potassium, sulfate, and chloride (9000 mg/L each), calcium, magnesium and iron (4000 mg/L each), nitrate (2000 mg/L), and cadmium, lead, copper, zinc, cobalt, and chromium (10 mg/L each) do not interfere.

NOTE 1—Background correction by techniques such as a continuum source, nonabsorbing lines, or chelation-extraction, may be necessary for low levels of nickel for some types of water. Instrument manufacturer's instructions for use of the specific correction technique should be followed.

## 10. Apparatus

10.1 *Atomic Absorption Spectrophotometer*, for use at 232.0 nm.

NOTE 2—The manufacturer's instructions should be followed for all instrumental parameters. Wavelengths other than 232.0 nm may be used if they have been determined to be equally suitable.

10.2 *Nickel Hollow-Cathode Lamp*—Multielement hollow-cathode lamps are available and also have been found satisfactory.

10.3 *Pressure-Reducing Valves*—The supplies of fuel and oxidant shall be maintained at pressures somewhat higher than the controlled operating pressure of the instrument by suitable valves.

## 11. Reagents and Materials

11.1 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl).

NOTE 3—If a high reagent blank is obtained, distill the HCl or use a spectrograde acid.

NOTE 4—When HCl is distilled, an azeotropic mixture is formed (~6 N HCl). Therefore, whenever concentrated HCl is used in the preparation of reagents or in the procedure, use twice the volume of the distilled HCl.

11.2 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (HNO<sub>3</sub>).

NOTE 5—If a high reagent blank is obtained, distill the HNO<sub>3</sub> or use a spectrograde acid.

11.3 *Nitric Acid* (1 + 499)—Add 1 volume HNO<sub>3</sub> (sp gr 1.42) to 499 volumes of water.

11.4 *Nickel Solution, Stock* (1.0 mL = 1.0 mg Ni)—Dissolve 4.953 g of nickelous nitrate [Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O] in a mixture of 10 mL of HNO<sub>3</sub> (sp gr 1.42) and 100 mL of water. Dilute to 1 L with water.

11.5 *Nickel Solution, Standard* (1 mL = 0.1 mg Ni)—Dilute 100.0 mL of the stock nickel solution and 1 mL of HNO<sub>3</sub> to 1 L with water.

### 11.6 Oxidant:

11.6.1 *Air*, which has been passed through a suitable filter to remove oil, water, and other foreign substances is the usual oxidant.

### 11.7 Fuel:

11.7.1 *Acetylene*—Standard, commercially available acetylene is the usual fuel. Acetone, always present in acetylene cylinders, can affect analytical results. The cylinder should be replaced at 50 psig (345 kPa). (**Warning**—“Purified” grade acetylene containing a special proprietary solvent rather than acetone should not be used with poly(vinyl chloride) tubing as weakening of the walls can cause a potentially hazardous situation.)

## 12. Standardization

12.1 Prepare a blank and at least four standard solutions to bracket the expected nickel concentration range of the samples to be analyzed by diluting the standard nickel solution with HNO<sub>3</sub>(1 + 499) as described in 11.5. Prepare the standards (100 mL) each time the test is to be performed.

12.2 For total recoverable nickel add 0.5 mL of HNO<sub>3</sub>(sp gr 1.42) and proceed as directed in 13.2 through 13.4. For dissolved nickel proceed with 13.5.

12.3 Atomize the blank and standards and record the instrument readings. Atomize HNO<sub>3</sub>(1 + 499) between each standard.

12.4 Prepare an analytical curve by plotting the absorbance versus the concentration for each standard on linear graph paper. Alternatively, read directly in concentration if this capability is provided with the instrument.

## 13. Procedure

13.1 Measure 100.0 mL of a well-mixed acidified sample into a 125-mL beaker or flask.

NOTE 6—If only dissolved nickel is to be determined, start with 13.5.

13.2 Add 5 mL of HCl (sp gr 1.19) to each sample.

13.3 Heat the samples on a steam bath or hotplate in a well-ventilated fume hood until the volume has been reduced to 15 to 20 mL, making certain that the samples do not boil.

NOTE 7—For samples with high levels of suspended matter or dissolved solids, the amount of reduction in volume is left to the discretion of the analyst.

13.4 Cool and filter the samples through a suitable filter, such as fine-textured, acid-washed, ashless paper, into 100-mL volumetric flasks. Wash the filter paper two or three times with water and bring filtrate to volume.

13.5 Atomize each filtered and acidified sample and determine its absorbance or concentration. Atomize HNO<sub>3</sub>(1 + 499) between samples.

## 14. Calculation

14.1 Calculate the concentration of nickel in each sample, in milligrams per litre, using 12.4.

**TABLE 1 Precision and Concentration, Direct Aspiration (Test Method A)**

<i>Reagent Water:</i>			
Concentration ( $\bar{X}$ ), mg/L	7.74	0.84	3.93
$S_T$	0.502	0.102	0.383
$S_O$	0.261	0.045	0.324
<i>Natural Water:</i>			
Concentration ( $\bar{X}$ ), mg/L	7.74	0.84	3.87
$S_T$	0.629	0.108	0.401
$S_O$	0.420	0.067	0.192

## 15. Precision and Bias <sup>9</sup>

15.1 The precision of this test method was tested by eleven laboratories in reagent water, natural waters, a refinery effluent and in a wastewater. Five laboratories reported data for two operators. The precision of this test method is shown in Table 1; the bias is shown in Table 2.

15.2 It is the user’s responsibility to ensure the validity of this test method for waters of untested matrices.

15.3 This section on precision and bias conforms to Practice D 2777 – 77 which was in place at the time of collaborative testing. Under the allowances made in 1.4 of D 2777 – 98, these precision and bias data do meet existing requirements of interlaboratory studies of Committee D19 test methods.

## 16. Quality Control

16.1 In order to be certain that analytical values obtained using these test methods are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when analyzing nickel.

### 16.2 Calibration and Calibration Verification

16.2.1 Analyze at least three working standards containing concentrations of nickel that bracket the expected sample concentration, prior to analysis of samples, to calibrate the instrument. The calibration correlation coefficient shall be equal to or greater than 0.990. In addition to the initial calibration blank, a calibration blank shall be analyzed at the end of the batch run to ensure contamination was not a problem during the batch analysis.

16.2.2 Verify instrument calibration after standardization by analyzing a standard at the concentration of one of the calibration standards. The concentration of a mid-range standard should fall within  $\pm 15\%$  of the known concentration.

16.2.3 If calibration cannot be verified, recalibrate the instrument.

### 16.3 Initial Demonstration of Laboratory Capability

16.3.1 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, and so forth, a precision and bias study must be performed to demonstrate laboratory capability.

16.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material containing a midrange concentration of nickel. The matrix and chemistry of the solution should be equivalent to the solution used in the collaborative study. Each replicate must be taken through the

<sup>9</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D19-1038.

**TABLE 2 Determination of Bias, Direct Aspiration  
(Test Method A)**

Amount Added, mg/L	Amount Found, mg/L	Bias, mg/L	Bias, %	Statistically Significant (95 % Confidence Level)
<i>Reagent Water:</i>				
8.0	7.74	-0.26	-3	yes
0.8	0.84	+0.04	+5	yes
4.0	3.93	-0.07	-2	no
<i>Natural Water:</i>				
8.0	7.74	-0.26	-3	yes
0.8	0.84	+0.04	+5	yes
4.0	3.87	-0.13	-3	yes

complete analytical test method including any sample preservation and pretreatment steps. The replicates may be interspersed with samples.

16.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in Table 1. This study should be repeated until the recoveries are within the limits given in Table 1. 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.

#### 16.4 Laboratory Control Sample (LCS)

16.4.1 To ensure that the test method is in control, analyze a LCS containing a known concentration of nickel with each batch or ten samples. If large numbers of samples are analyzed in the batch, analyze the LCS after every ten samples. The laboratory control samples for a large batch should cover the analytical range when possible. The LCS must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The result obtained for a mid-range LCS shall fall within  $\pm 15\%$  of the known concentration.

16.4.2 If the result is not within these limits, analysis of samples is halted until the problem is corrected, and either all the 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.

#### 16.5 Method Blank

16.5.1 Analyze a reagent water test blank with each batch. The concentration of nickel found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of nickel is found above this level, analysis of samples is halted until the contamination is eliminated, and a blank shows no contamination at or above this level, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

#### 16.6 Matrix Spike (MS)

16.6.1 To check for interferences in the specific matrix being tested, perform a MS on at least one sample from each batch by spiking an aliquot of the sample with a known concentration of nickel and taking it through the analytical method.

16.6.2 The spike concentration plus the background concentration of nickel must not exceed the high calibration standard.

The spike must produce a concentration in the spiked sample that is 2 to 5 times the analyte concentration in the unspiked sample, or 10 to 50 times the detection limit of the test method, whichever is greater.

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

$$P = 100[A(V_s + V) - BV_s] / CV$$

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.

16.6.4 The percent recovery of the spike shall fall within the limits, based on the analyte concentration, listed in Test Method D 5810, Table 1. 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: the matrix interference must be removed, all samples in the batch must be analyzed by a test method not affected by the matrix interference, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

NOTE 8—Acceptable spike recoveries are dependent on the concentration of the component of interest. See Test Method D 5810 for additional information.

#### 16.7 Duplicate

16.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each batch. If the concentration of the analyte is less than five times the detection limit for the analyte, a matrix spike duplicate (MSD) should be used.

16.7.2 Calculate the standard deviation of the duplicate values and compare to the precision in the collaborative study using an F test. Refer to 6.4.4 of Practice D 5847 for information on applying the F test.

16.7.3 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.

#### 16.8 Independent Reference Material (IRM)

16.8.1 In order to verify the quantitative value produced by the test method, analyze an Independent Reference Material (IRM) submitted as a regular sample (if practical) to the laboratory at least once per quarter. The concentration of the IRM should be in the concentration mid-range for the method chosen. The value obtained must fall within the control limits established by the laboratory.

## TEST METHOD B—ATOMIC ABSORPTION, CHELATION-EXTRACTION

### 17. Scope

17.1 This test method covers the determination of dissolved and total recoverable nickel and has been used successfully with reagent water, tap water, river water, artificial seawater and a synthetic (NaCl) brine.

17.2 This test method is applicable in the range from 10 to 1000  $\mu$ g/L of nickel. The range may be extended upward by dilution of the sample.

## 18. Summary of Test Method

18.1 Nickel is determined by atomic absorption spectrophotometry. The element, either dissolved or total recoverable, is chelated with pyrrolidine dithiocarbamic acid and extracted with chloroform. The extract is evaporated to dryness, treated with hot nitric acid to destroy organic matter, dissolved in hydrochloric acid, and diluted to a specified volume with water. The resulting solution is then aspirated into the air-acetylene flame of the spectrophotometer. The digestion procedure summarized in 8.1 is used for total recoverable nickel. The same chelation-extraction procedure is used for cadmium (Test Methods D 3557), cobalt (Test Methods D 3558), copper (Test Methods D 1688), iron (Test Methods D 1068), lead (Test Methods D 3559), and zinc (Test Methods D 1691).

## 19. Interferences

19.1 See 9.1.

## 20. Apparatus

20.1 All apparatus described in Section 10 are required.

## 21. Reagents and Materials

21.1 *Bromphenol Blue Indicator Solution* (1 g/L)—Dissolve 0.1 g of bromphenol blue in 100 mL of 50 % ethanol or isopropanol.

21.2 *Chloroform* ( $\text{CHCl}_3$ ).

21.3 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl) (see Note 5).

21.4 *Hydrochloric Acid* (1+2)—Add 1 volume of hydrochloric acid (HCl), sp gr 1.19, to 2 volumes of water.

21.5 *Hydrochloric Acid* (1+49)—Add 1 volume of hydrochloric acid (HCl), sp gr 1.19, to 49 volumes of water.

21.6 *Nickel Solution, Stock* (1.0 mL = 200  $\mu$ g Ni)—Dissolve 0.9906 g of nickelous nitrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) in water containing 1 mL of  $\text{HNO}_3$  (sp gr 1.42) and dilute to 1 L with water.

21.7 *Nickel Solution, Standard* (1.0 mL = 2.0  $\mu$ g Ni)—Dilute 10.0 mL of nickel solution, stock and 1 mL of  $\text{HNO}_3$  (sp gr 1.42) to 1 L with water. This standard is used to prepare working standards at the time of analysis.

21.8 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid ( $\text{HNO}_3$ ) (see Note 5).

21.9 *Pyrrolidine Dithiocarbamic Acid-Chloroform Reagent*—Add 36 mL of pyrrolidine to 1 L of  $\text{CHCl}_3$ . Cool the solution and add 30 mL of  $\text{CS}_2$  in small portions, swirling between additions. Dilute to 2 L with  $\text{CHCl}_3$ . The reagent can be used for several months if stored in a cool, dark place. (**Warning**—All components of this reagent are highly toxic. Carbon disulfide is also highly flammable. Prepare and use in a well-ventilated hood. Avoid inhalation and direct contact.)

21.10 *Sodium Hydroxide Solution* (100 g/L)—Dissolve 100 g of sodium hydroxide (NaOH) in water and dilute to 1 L.

21.11 *Reagents and Materials*—See Section 11.

21.12 *Oxidant*—See 11.6.

21.13 *Fuel*—See 11.7.

## 22. Standardization

22.1 Prepare a blank and sufficient standard containing from 0.0 to 100  $\mu$ g of nickel by diluting 0.0 to 50.0-mL portions of nickel standard solution to 100 mL with water (see 21.7).

22.2 For total recoverable nickel use 125-mL beakers or flasks, add 0.5 mL of  $\text{HNO}_3$  (sp gr 1.42) and proceed as directed in 23.2 through 23.15. For dissolved nickel use 250-mL separatory funnels and proceed as directed in 23.5 through 23.15. All samples and standards should be treated the same.

22.3 Construct an analytical curve by plotting the absorbances of standards versus micrograms of nickel. Alternatively, read directly in concentration if this capability is provided with the instrument.

## 23. Procedure

23.1 Measure a volume of a well-mixed acidified sample containing less than 100  $\mu$ g of nickel (100-mL maximum) into a 125-mL beaker or flask and adjust the volume to 100 mL with water.

NOTE 9—If only dissolved nickel is to be determined measure a volume of filtered and acidified sample containing less than 10.0  $\mu$ g of nickel (100-mL maximum) into a 250-mL separatory funnel, and start with 23.5.

23.2 Add 5 mL of HCl (sp gr 1.19) to each sample.

23.3 Heat the samples on a steam bath or hotplate until the volume has been reduced to 15 to 20 mL, making certain that the samples do not boil.

NOTE 10—For brines and samples with high levels of suspended matter, the amount of reduction in volume is left to the discretion of the analyst.

23.4 Cool and filter the samples through a suitable filter, such as fine-textured, acid-washed, ashless paper into 250-mL separatory funnels. Wash the filter paper two or three times with water and bring to about 100 mL of volume.

23.5 Add 2 drops of bromphenol blue indicator solution and mix.

23.6 Adjust the pH by addition of NaOH (100 g/L) solution until a blue color persists. Add HCl (1 + 49) by drops until the blue color just disappears; then add 2.5 mL of HCl (1 + 49) in excess. The pH at this point should be 2.3.

NOTE 11—The pH adjustment in 23.6 may be made with a pH meter instead of using an indicator.

23.7 Add 10 mL of pyrrolidine dithiocarbamic acid-chloroform reagent and shake vigorously for 2 min (**Warning**—All components of this reagent are highly toxic. Carbon disulfide is also highly flammable. Prepare and use in a well-ventilated hood. Avoid inhalation and direct contact.)

23.8 Plug the tip of the separatory funnel with cotton, allow the phases to separate, and drain the  $\text{CHCl}_3$  phase into a 100-mL beaker.

23.9 Repeat the extraction with 10 mL of  $\text{CHCl}_3$  and drain the  $\text{CHCl}_3$  layer into the same beaker.

NOTE 12—If color still remains in the  $\text{CHCl}_3$  extract, reextract the aqueous phase until the  $\text{CHCl}_3$  layer is colorless.

23.10 Place the beaker on a hotplate set at low heat or on a steam bath, and evaporate to near dryness. Remove beaker

**TABLE 3 Precision and Concentration, Chelation–Extraction (Test Method B)**

<i>Reagent Water:</i>			
Concentration (X), μ g/L	784.2	56.8	398.5
$S_T$	146.4	15.2	35.1
$S_O$	41.02	9.18	22.97
<i>Natural Water:</i>			
Concentration (X), μ g/L	794.4	53.6	399.4
$S_T$	133.9	11.2	37.7
$S_O$	70.9	12.6	11.1

from heat and allow residual solvent to evaporate without further heating. (**Warning**—Perform in a well-ventilated hood.)

23.11 Hold the beaker at a 45° angle and slowly add dropwise 2 mL of HNO<sub>3</sub>(sp gr 1.42), rotating the beaker to effect thorough contact of the acid with the residue.

23.11.1 If acid is added to the beaker in a vertical position, a violent reaction will occur accompanied by high heat and spattering.

23.12 Place the beaker on a hotplate set at low heat in a well-ventilated hood, or on a steam bath, and evaporate to near dryness. Remove beaker from heat and allow residual solvent to evaporate without further heating.

23.13 Add 2 mL of HCl (1+2) to the beaker, and heat, while swirling for 1 min.

NOTE 13—If a precipitate appears when the hydrochloric acid (1+2) is added to the dried residue, obtain a fresh supply of pyrrolidine which has a different lot number or redistill the pyrrolidine just before preparing the pyrrolidine dithiocarbamic acid-chloroform reagent (20.9).

23.14 Cool and quantitatively transfer the solution to a 10-mL volumetric flask and bring to volume with water.

23.15 Aspirate each sample and record the scale reading or concentration.

## 24. Calculation

24.1 Determine the weight of nickel in each sample by referring to 22.3. Calculate the concentration of nickel in micrograms per litre as follows:

$$\text{Nickel, } \mu\text{g/L} = (1000/A) \times B$$

where:

$A$  = volume of original sample, mL, and

$B$  = weight of nickel sample, μg.

## 25. Precision and Bias <sup>5</sup>

25.1 The precision of this test method was tested by six laboratories in reagent water, natural waters and in synthetic brines. One laboratory reported data from two operators. The precision of this test method is shown in Table 3; the bias is shown in Table 4.

25.2 It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

25.3 This section on precision and bias conforms to Practice D 2777 – 77 which was in place at the time of collaborative testing. Under the allowances made in 1.4 of D 2777 – 98, these precision and bias data do meet existing requirements of interlaboratory studies of Committee D19 test methods.

**TABLE 4 Determination of Bias, Chelation-Extraction (Test Method B)**

Amount Added, μg/L	Amount Found, μg/L	Bias, μg/L	Bias, %	Statistically Significant (95 % Confidence Level)
<i>Reagent Water:</i>				
900	784.2	-115.8	-12.9	yes
50	56.8	+ 6.8	+ 13.6	no
400	398.5	-1.5	-0.4	no
<i>Natural Water:</i>				
900	794.4	-105.6	-11.7	yes
50	53.6	+ 3.6	+ 7.2	no
400	399.4	-0.6	-0.2	no

## 26. Quality Control

26.1 In order to be certain that analytical values obtained using these test methods are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when analyzing nickel.

### 26.2 Calibration and Calibration Verification

26.2.1 Analyze at least three working standards containing concentrations of nickel that bracket the expected sample concentration, prior to analysis of samples, to calibrate the instrument. The calibration correlation coefficient shall be equal to or greater than 0.990. In addition to the initial calibration blank, a calibration blank shall be analyzed at the end of the batch run to ensure contamination was not a problem during the batch analysis.

26.2.2 Verify instrument calibration after standardization by analyzing a standard at the concentration of one of the calibration standards. The concentration of a mid-range standard should fall within ±15% of the known concentration.

26.2.3 If calibration cannot be verified, recalibrate the instrument.

### 26.3 Initial Demonstration of Laboratory Capability

26.3.1 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, and so forth, a precision and bias study must be performed to demonstrate laboratory capability.

26.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material containing a midrange concentration of nickel. The matrix and chemistry of the solution should be equivalent to the solution used in the collaborative study. 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.

26.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in Table 1. This study should be repeated until the recoveries are within the limits given in Table 1. 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.

### 26.4 Laboratory Control Sample (LCS)

26.4.1 To ensure that the test method is in control, analyze a LCS containing a known concentration of nickel with each batch or ten samples. If large numbers of samples are analyzed in the batch, analyze the LCS after every ten samples. The laboratory control samples for a large batch should cover the analytical range when possible. The LCS must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The result obtained for a mid-range LCS shall fall within  $\pm 15\%$  of the known concentration.

26.4.2 If the result is not within these limits, analysis of samples is halted until the problem is corrected, and either all the 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.

#### 26.5 Method Blank

26.5.1 Analyze a reagent water test blank with each batch. The concentration of nickel found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of nickel is found above this level, analysis of samples is halted until the contamination is eliminated, and a blank shows no contamination at or above this level, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

#### 26.6 Matrix Spike (MS)

26.6.1 To check for interferences in the specific matrix being tested, perform a MS on at least one sample from each batch by spiking an aliquot of the sample with a known concentration of nickel and taking it through the analytical method.

26.6.2 The spike concentration plus the background concentration of nickel must not exceed the high calibration standard. The spike must produce a concentration in the spiked sample that is 2 to 5 times the analyte concentration in the unspiked sample, or 10 to 50 times the detection limit of the test method, whichever is greater.

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

$$P = 100[A(V_s + V) - BV_s] / CV$$

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.

26.6.4 The percent recovery of the spike shall fall within the limits, based on the analyte concentration, listed in Test Method D 5810, Table 1. 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: the matrix interference must be removed, all samples in the batch must be analyzed by a test method not affected by the matrix interference, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

NOTE 14—Acceptable spike recoveries are dependent on the concen-

tration of the component of interest. See Test Method D 5810 for additional information.

#### 26.7 Duplicate

26.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each batch. If the concentration of the analyte is less than five times the detection limit for the analyte, a matrix spike duplicate (MSD) should be used.

26.7.2 Calculate the standard deviation of the duplicate values and compare to the precision in the collaborative study using an F test. Refer to 6.4.4 of Practice D 5847 for information on applying the F test.

26.7.3 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.

#### 26.8 Independent Reference Material (IRM)

26.8.1 In order to verify the quantitative value produced by the test method, analyze an Independent Reference Material (IRM) submitted as a regular sample (if practical) to the laboratory at least once per quarter. The concentration of the IRM should be in the concentration mid-range for the method chosen. The value obtained must fall within the control limits established by the laboratory.

## TEST METHOD C—ATOMIC ABSORPTION, GRAPHITE FURNACE

### 27. Scope

27.1 This test method covers the determination of dissolved and total recoverable nickel and has been used successfully with reagent grade water, lake water, river water, well and filtered tap water, and a condensate from a medium Btu coal gasification process. It is the user's responsibility to ensure the validity of this test method to other matrices.

27.2 This test method is applicable in the range from approximately 5 to 100  $\mu\text{g/L}$  nickel using a 20- $\mu\text{L}$  injection. The range can be increased or decreased by varying the volume of sample injected or the instrumental settings. High concentrations may be diluted but preferably should be analyzed by direct aspiration atomic absorption spectrophotometry (see Test Method A).

27.3 The analyst is encouraged to consult Practice D 3919 for a general discussion of interferences and sample analysis procedures for graphite furnace atomic absorption spectrophotometry.

### 28. Summary of Test Method

28.1 Nickel is determined by an atomic absorption spectrophotometer used in conjunction with a graphite furnace. A sample is placed in a graphite tube, evaporated to dryness, charred (pyrolyzed or ashed) and atomized. The absorption signal generated during atomization is recorded and compared to standards. A general guide for the application of the graphite furnace is given in Practice D 3919.

28.2 Dissolved nickel is determined on a filtered sample with no pretreatment.

28.3 Total recoverable nickel is determined following acid digestion and filtration. Because chlorides interfere with furnace procedures for some metals, the use of hydrochloric acid

in any digestion or solubilization step is to be avoided. If suspended material is not present, this digestion and filtration may be omitted.

### 29. Interferences

29.1 For a complete discussion on general interferences with furnace procedures, the analyst is referred to Practice D 3919.

29.2 The following interferences have been reported at the indicated levels:

Nickel, µg/L	Concomitant Added, mg/L	% Error
42	10 Fe (Cl)	+23.8
42	100 Fe (Cl)	+66.7
72	10 Cu (O)	+12.5
72	100 Cu (O)	+13.9

### 30. Apparatus

30.1 *Atomic Absorption Spectrophotometer*, for use at 232.0 nm with background correction.

NOTE 15—A wavelength other than 232.0 nm may be used if it has been determined to be suitable. Greater linearity may be obtained at high concentrations by using a less sensitive wavelength.

NOTE 16—The manufacturer's instructions should be followed for all instrumental parameters.

30.2 *Nickel Hollow-Cathode Lamp*, a single-element lamp is preferred, but multielement lamps may be used.

30.3 *Graphite Furnace*, capable of reaching temperatures sufficient to atomize the element of interest.

30.4 *Graphite Tubes*, compatible with furnace device. Pyrolytically coated graphite tubes are recommended to eliminate the possible formation of carbides.

30.5 *Pipets*, microlitre with disposable tips. Sizes may range from 1 to 100 µL, as required.

30.6 *Data Storage and Reduction Devices, Computer- and Microprocessor-Controlled Devices, or Strip Chart Recorders* shall be utilized for collection, storage, reduction, and problem recognition (such as drift, incomplete atomization, changes in sensitivity, etc.). Strip chart recorders shall have a full scale deflection time of 0.2 s or less to ensure accuracy.

30.7 *Automatic Sampling*, recommended if available.

### 31. Reagents and Materials

31.1 *Nickel Solution, Standard* (1.0 mL = 1.0 µg Ni)—Dilute 5.0 mL of nickel solution, stock (see 31.2) and 1 mL of HNO<sub>3</sub>(sp gr 1.42) to 1 L with water. This standard is used to prepare working standards at the time of the analysis.

31.2 *Nickel Solution, Stock* (1.0 mL = 200 µg Ni)—(See 21.6.)

31.3 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (HNO<sub>3</sub>) (see Note 5).

31.4 *Argon*, standard, welders grade, commercially available. Nitrogen may also be used if recommended by the instrument manufacturer.

### 32. Standardization

32.1 Initially, set the instrument according to the manufacturer's specifications. Follow the general instructions as provided in Practice D 3919.

**TABLE 5 Determination of Bias and Overall Precision in Reagent Water (Test Method C)**

Amount Added, µg/L	Amount Found, µg/L	S <sub>T</sub>	\Bias, µg/L	Bias, %	Statistically Significant
80	87.0	12.97	+ 7.0	+ 8.8	no
8.0	9.37	2.11	+ 1.37	+ 17.1	yes
30	31.6	5.49	+ 1.6	+ 5.3	no

### 33. Procedure

33.1 Clean all glassware to be used for preparation of standard solutions or in the solubilization step, or both, by rinsing first with HNO<sub>3</sub>(1 + 1) and then with water.

33.2 Measure 100.0 mL of each standard and well-mixed sample into 125-mL beakers or flasks. For total recoverable nickel add HNO<sub>3</sub>(sp gr 1.42) to each standard and sample at a rate of 5 mL/L and proceed as directed in 33.4 through 33.6.

33.3 If only dissolved nickel is to be determined, filter the sample through a 0.45-µm membrane filter prior to acidification and proceed to 33.6.

33.4 Heat the samples at 95°C on a steam bath or hotplate in a well-ventilated fume hood until the volume has been reduced to 15 to 20 mL, making certain that the samples do not boil (see Note 7).

33.5 Cool and filter the sample through a suitable filter (such as fine-textured, acid-washed, ashless paper) into a 100-mL volumetric flask. Wash the filter paper two or three times with water and bring to volume (see Note 17). The acid concentration at this point should be 0.5 % HNO<sub>3</sub>.

NOTE 17—If suspended material is not present, this filtration may be omitted, but the sample must still be diluted to 100 mL.

33.6 Inject a measured aliquot of the sample into the furnace device following the directions as provided by the particular instrument manufacturer. Refer to Practice D 3919.

### 34. Calculation

34.1 Determine the concentration of nickel in each sample by referring to Practice D 3919.

### 35. Precision and Bias<sup>10</sup>

35.1 The precision of this test method was tested by 12 laboratories in reagent water, lake water, river water, well water, filtered tap water, and condensate from a medium Btu coal gasification process. Two laboratories reported data from two operators. Although multiple injections may have been made, the report sheets provided allowed only for reporting single values. Thus, no single-operator precision data can be calculated. Bias data and overall precision data are given in Table 5 and Table 6.

35.2 These data may not apply to waters of other matrices, therefore, it is the responsibility of the analyst to ensure the validity of this test method for waters of untested matrices.

<sup>10</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D19-1107.

**TABLE 6 Determination of Bias and Overall Precision in Water of Choice (Test Method C)**

Amount Added, µg/L	Amount Found, µg/L	$S_T$	Bias, µg/L	Bias, %	Statistically Significant
80	81.0	9.42	+1.0	+1.3	no
8.0	7.58	1.54	-0.42	-5.3	no
30	30.8	5.29	+0.8	+2.7	no

35.3 This section on precision and bias conforms to Practice D 2777 – 77 which was in place at the time of collaborative testing. Under the allowances made in 1.4 of D 2777 – 98, these precision and bias data do meet existing requirements of interlaboratory studies of Committee D19 test methods.

### 36. Quality Control

36.1 In order to be certain that analytical values obtained using these test methods are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when analyzing nickel.

#### 36.2 Calibration and Calibration Verification

36.2.1 Analyze at least three working standards containing concentrations of nickel that bracket the expected sample concentration, prior to analysis of samples, to calibrate the instrument. The calibration correlation coefficient shall be equal to or greater than 0.990. In addition to the initial calibration blank, a calibration blank shall be analyzed at the end of the batch run to ensure contamination was not a problem during the batch analysis.

36.2.2 Verify instrument calibration after standardization by analyzing a standard at the concentration of one of the calibration standards. The concentration of a mid-range standard should fall within  $\pm 15\%$  of the known concentration.

36.2.3 If calibration cannot be verified, recalibrate the instrument.

#### 36.3 Initial Demonstration of Laboratory Capability

36.3.1 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, and so forth, a precision and bias study must be performed to demonstrate laboratory capability.

36.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material containing a midrange concentration of nickel. The matrix and chemistry of the solution should be equivalent to the solution used in the collaborative study. 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.

36.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in Table 1. This study should be repeated until the recoveries are within the limits given in Table 1. 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.

#### 36.4 Laboratory Control Sample (LCS)

36.4.1 To ensure that the test method is in control, analyze a LCS containing a known concentration of nickel with each batch or ten samples. If large numbers of samples are analyzed in the batch, analyze the LCS after every ten samples. The laboratory control samples for a large batch should cover the analytical range when possible. The LCS must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The result obtained for a mid-range LCS shall fall within  $\pm 15\%$  of the known concentration.

36.4.2 If the result is not within these limits, analysis of samples is halted until the problem is corrected, and either all the 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.

#### 36.5 Method Blank

36.5.1 Analyze a reagent water test blank with each batch. The concentration of nickel found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of nickel is found above this level, analysis of samples is halted until the contamination is eliminated, and a blank shows no contamination at or above this level, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

#### 36.6 Matrix Spike (MS)

36.6.1 To check for interferences in the specific matrix being tested, perform a MS on at least one sample from each batch by spiking an aliquot of the sample with a known concentration of nickel and taking it through the analytical method.

36.6.2 The spike concentration plus the background concentration of nickel must not exceed the high calibration standard. The spike must produce a concentration in the spiked sample that is 2 to 5 times the analyte concentration in the unspiked sample, or 10 to 50 times the detection limit of the test method, whichever is greater.

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

$$P = 100[A(V_s + V) - BV_s] / CV$$

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.

36.6.4 The percent recovery of the spike shall fall within the limits, based on the analyte concentration, listed in Test Method D 5810, Table 1. 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: the matrix interference must be removed, all samples in the batch must be analyzed by a test method not affected by the matrix interference, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

NOTE 18—Acceptable spike recoveries are dependent on the concentration of the component of interest. See Test Method D 5810 for additional information.

### 36.7 Duplicate

36.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each batch. If the concentration of the analyte is less than five times the detection limit for the analyte, a matrix spike duplicate (MSD) should be used.

36.7.2 Calculate the standard deviation of the duplicate values and compare to the precision in the collaborative study using an F test. Refer to 6.4.4 of Practice D 5847 for information on applying the F test.

36.7.3 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.

### 36.8 Independent Reference Material (IRM)

36.8.1 In order to verify the quantitative value produced by the test method, analyze an Independent Reference Material (IRM) submitted as a regular sample (if practical) to the laboratory at least once per quarter. The concentration of the IRM should be in the concentration mid-range for the method chosen. The value obtained must fall within the control limits established by the laboratory.

## 37. Keywords

37.1 atomic absorption; chelation; graphite furnace; nickel; water

## APPENDIX

### (Nonmandatory Information)

#### X1. RATIONALE FOR DISCONTINUATION OF TEST METHODS

X1.1 Colorimetric Test Methods (Former Test Method A—Carbamate, and Former Test Method B—Glyoxime):

X1.1.1 These test methods were discontinued in 1988. They may be found published in their entirety in the 1988 Annual Book of ASTM Standards, Vol 11.01.

X1.1.2 These test methods cover the determination of nickel in water for samples containing 0.001 to 0.05 mg/L of nickel (carbamate test method) or 0.01 to 5.0 mg/L of nickel (glyoxime test method).

X1.1.3 Summary of Test Methods:

X1.1.3.1 *Carbamate*—This test method is based on the formation of a yellow-green complex of nickel with sodium diethyldithiocarbamate, at a pH of 8.5 to 9.0 in the presence of citrate. The color complex is extracted with carbon tetrachloride and the color intensity measured by means of a spectrophotometer. Correction is made for copper up to 0.100 mg/L. Calculations are based on absorbance measurements at wavelengths of 328 and 436 nm.

X1.1.3.2 *Glyoxime*—This test method is based on the formation of a wine-red color complex of nickel with ammoniacal dimethylglyoxime in the presence of iodine. The color is measured directly with a filter photometer or a spectrophotometer.

X1.1.4 These test methods were discontinued because there were insufficient laboratories interested in participating in a collaborative study to obtain the necessary precision and bias data as required by Practice D 2777.

## SUMMARY OF CHANGES

Committee D19 has identified the location of selected changes to this standard since the last issue (D 1886–94 (1998)) that may impact the use of this standard.

- (1) Sections 15.3, 25.3, and 35.3 were added.
- (2) The QC Sections 16, 26, and 36 were added to the test method.

- (3) All sections after Section 15 were renumbered.

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