**Designation: D 3558 – 03**

# Standard Test Methods for
# Cobalt in Water [1]

This standard is issued under the fixed designation D 3558; 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.

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

## 1. Scope*

1.1 These test methods cover the determination of dissolved and total recoverable cobalt in water and wastewater [2] by atomic absorption spectrophotometry. Three test methods are included as follows:

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

1.2 Test Method A has been used successfully with reagent water, potable water, river water, and wastewater. Test Method B has been used successfully with reagent water, potable water, river water, sea water and brine. Test Method C was successfully evaluated in reagent water, artificial seawater, river water, tap water, and a synthetic brine. It is the analyst'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 hazard statements, see 11.7.1, 21.10, and 23.10.

## 2. Referenced Documents

2.1 *ASTM Standards:*
D 858 Test Methods for Manganese in Water [3]
D 1066 Practice for Sampling Steam [3]
D 1068 Test Methods for Iron in Water [3]
D 1129 Terminology Relating to Water [3]
D 1193 Specification for Reagent Water [3]
D 1687 Test Methods for Chromium in Water [3]

D 1688 Test Methods for Copper in Water [3]
D 1691 Test Methods for Zinc in Water [3]
D 1886 Test Methods for Nickel in Water [3]
D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D19 on Water [3]
D 3370 Practices for Sampling Water from Closed Conduits [3]
D 3557 Test Methods for Cadmium in Water [3]
D 3559 Test Methods for Lead in Water [3]
D 3919 Practice for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry [3]
D 4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents [3]
D 5810 Guide for Spiking into Aqueous Samples [3]
D 5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis [4]

## 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 cobalt*—an arbitrary analytical term relating to the recoverable forms of cobalt that are determinable by the digestion method which is included in the procedure.

## 4. Significance and Use

4.1 Most waters rarely contain more than trace concentrations of cobalt from natural sources. Although trace amounts of cobalt seem to be essential to the nutrition of some animals, large amounts have pronounced toxic effects on both plant and animal life.

## 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

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

Reagents of the American Chemical Society where such specifications are available. [5] 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, reference 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 specified at the time of the round-robin testing of this test method.

## 6. Sampling

6.1 Collect the samples in accordance with Practices D 3370 and Practice D 1066, as applicable.

6.2 Preserve samples with $HNO_3$ (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 cobalt is to be determined, filter the sample through a 0.45-µm 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 cobalt in most waters and waste waters. It is the user's responsibility to ensure the validity of this test method in a particular matrix.

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

## 8. Summary of Test Method

8.1 Cobalt is determined by atomic absorption spectrophotometry. Dissolved cobalt is determined by aspirating a portion of the filtered sample directly with no pretreatment. Total recoverable cobalt is determined by aspirating the sample following hydrochloric-nitric acid digestion and filtration. The same digestion procedure may be used to determine total recoverable nickel (Test Methods D 1886), chromium (Test Methods D 1687), cadmium (Test Methods D 3557), copper (Test Methods D 1688), iron (Test Methods D 1068), lead (Test Methods D 3559), manganese (Test Methods D 858), zinc (Test Methods D 1691).

## 9. Interferences

9.1 Nitrate reportedly interferes at 1 mg/L by suppressing the absorption of the cobalt. This interference can be eliminated by adding 18 000 mg/L of ammonium chloride to blanks, standards, and samples.

9.2 Other metals usually do not interfere in the determination of cobalt by increasing or decreasing the amount of absorbed radiation. The most common interference is caused by a chemical reaction in the flame that prevents conversion of the cobalt to the atomic state.

9.3 Sodium, potassium, and sulfate, magnesium (4500 mg/L), iron (4000 mg/L), and nickel, lead, copper, zinc, cadmium, and chromium (10 mg/L each) do not interfere.

9.4 Background correction or a chelation-extraction procedure (see Test Method B) may be necessary to determine low levels of cobalt in some water.

NOTE 1—Instrument manufacturers' instructions for use of the specific correction technique should be followed.

## 10. Apparatus

10.1 *Atomic Absorption Spectrophotometer*, for use at 240.7 nm.

NOTE 2—The manufacturer's instructions should be followed for all instrumental parameters. A wavelength other than 240.7 nm may be used if it has been determined to be equally suitable.

10.2 *Cobalt Hollow-Cathode Lamps*—Multielement hollow-cathode lamps.

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 *Cobalt Solution, Stock* (1 mL = 1.0 mg Co)—Dissolve 4.0372 g of cobaltous chloride ($CoCl_2 \cdot 6H_2O$) in reagent water and dilute to 1 L.

11.2 *Cobalt Solution, Standard* (1 mL = 0.1 mg Co)—Dissolve 100.0 mL of the stock cobalt solution to 1 L with water.

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

NOTE 3—If a high reagent blank is obtained, distill the HCl or use spectrograde acid. When HCl is distilled, an azeotrophic mixture is obtained (approximately 6 *N* HCl is formed). Therefore, whenever concentrated HCl is specified for the preparation of a reagent or in the procedure, use double the volume specified if distilled acid is used.

11.4 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid ($HNO_3$).

NOTE 4—If a high reagent blank is obtained, distill the $HNO_3$ or use a spectrograde acid.

11.5 *Nitric Acid* (1 + 499)—Add 1 volume of $HNO_3$ (sp gr 1.42) to 499 volumes of 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

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[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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.
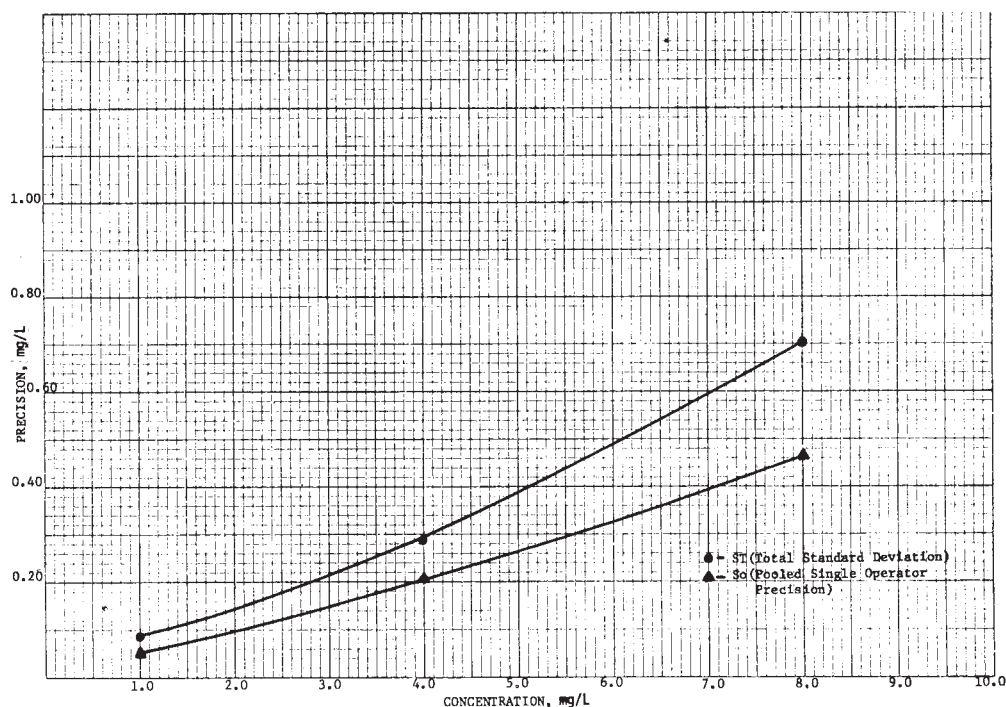
FIG. 1 Precision for Cobalt in Reagent Water, Type II by Direct Atomic Absorption

acetone should not be used with poly(vinyl chloride) tubing as weakening of the tubing walls can cause a potentially hazardous situation.)

## 12. Standardization

12.1 Prepare 100 mL each of a blank and at least four standard solutions to bracket the expected cobalt concentration range of the samples to be analyzed by diluting the standard cobalt solution (see 11.2) with $HNO_3$ (1 + 499). Prepare the standards each time the test is to be performed.

12.2 When determining total recoverable cobalt, add 0.5 mL of $HNO_3$ (sp gr 1.42) and proceed as directed in 13.2 through 13.4. When determining dissolved cobalt, proceed with 12.3.

12.3 Aspirate the blank and the standards and record the instrument readings. Aspirate $HNO_3$ (1 + 499) between standards.

12.4 Prepare an analytical curve by plotting the absorbance versus 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 5—If only dissolved cobalt is to be determined, proceed from 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 hood until the volume has been reduced to 15 to 20 mL, making certain that the samples do not boil.

NOTE 6—For samples with high levels of suspended matter, 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-texture, acid-washed, ashless paper, into 100-mL volumetric flasks. Wash the filter paper two or three times with water and bring to volume.

13.5 Atomize each filtered and acidified sample and determine its absorbance or concentration. Atomize $HNO_3$ (1 + 499) between samples.

## 14. Calculation

14.1 Calculate the concentration of cobalt in the sample, in milligrams per litre, using an analytical curve or, alternatively, read directly in concentration (see 12.4).

## 15. Precision and Bias [6]

15.1 The single-operator and overall precision of this test method within its designated range for eleven laboratories, which include a total of sixteen operators (at 1.0, 4.0, and 8.0 mg/L) analyzing each sample on three different days varies with the quantity being tested in accordance with Fig. 1 and Fig. 2.

15.2 Recoveries of known amounts of cobalt in a series of prepared standards for the same laboratories were as shown in Table 1.

15.3 These precision and bias data may not apply to waters of different matrices. The waters used in evaluations were reagent water, potable water, river water, and wastewater. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

15.4 This section on precision and bias conforms to Practice D 2777 – 77 which was in place at the time of collaborative

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[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D19–1032.
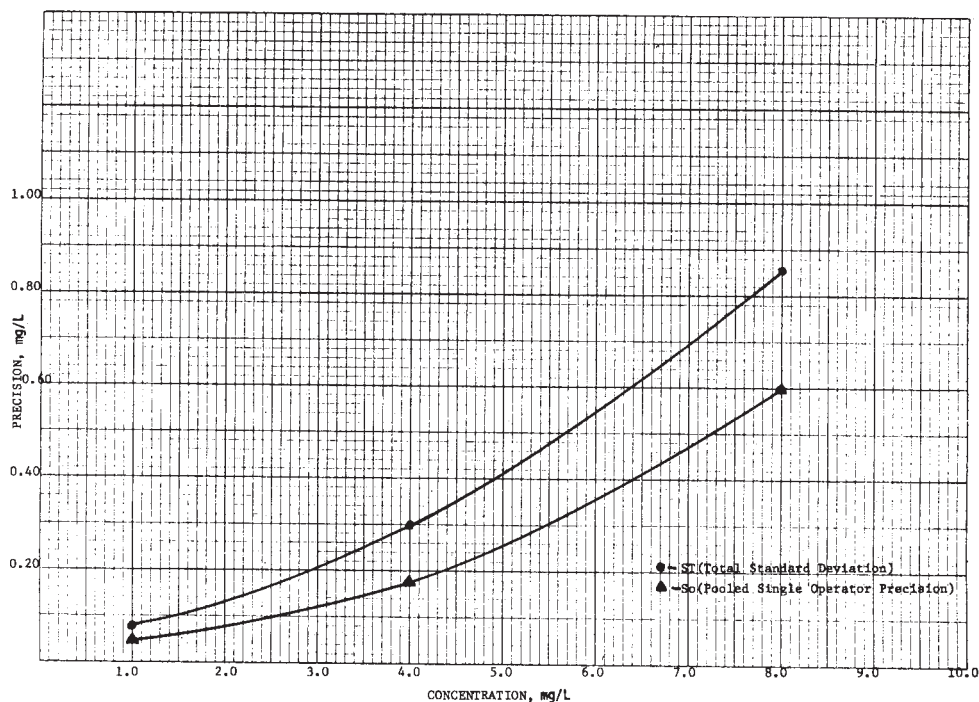
FIG. 2 Precision for Cobalt in Water of Choice by Direct Atomic Absorption

TABLE 1 Recoveries of Known Amounts of Cobalt Atomic Absorption, Direct

| | Amount Added, mg/L | Amount Found, mg/L | Bias, % | Statistically Significant (95 % Confidence Level) |
|---|---|---|---|---|
| Reagent water, Type II | 1.00 | 1.03 | +3.00 | Yes |
| | 4.00 | 3.98 | −0.50 | No |
| | 8.00 | 8.00 | 0.00 | No |
| Water of choice | 1.00 | 1.01 | +1.00 | No |
| | 4.00 | 4.01 | +0.25 | No |
| | 8.00 | 8.12 | +1.50 | No |

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 cobalt.

16.2 *Calibration and Calibration Verification*

16.2.1 Analyze at least three working standards containing concentrations of cobalt 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 ±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 cobalt. 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.

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 cobalt with each batch or 10 samples. If large numbers of samples are analyzed in the batch, analyze the LCS after every 10 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 ±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 cobalt found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of cobalt 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 cobalt and taking it through the analytical method.

16.6.2 The spike concentration plus the background concentration of cobalt 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:

$$P = [A(V_s + V) - BV_s] / CV \qquad (1)$$

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.

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 7—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 cobalt in most waters and brines. It is the user's responsibility to ensure the validity of this test method in a particular matrix.

17.2 This test method is applicable in the range from 10 to 1000µ g/L of cobalt. The range may be extended to concentrations greater than 1000 µg/L by dilution of the samples.

**18. Summary of Test Method**

18.1 Cobalt 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 HCl, and diluted to a specified volume with water. A portion of the resulting solution is then aspirated into the air-acetylene flame of the spectrophotometer. The digestion procedure summarized in 8.1 is used to determine total recoverable cobalt. The same chelation-extraction procedure may be used to determine nickel (Test Methods D 1886), chromium (Test Methods D 1687), 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 Section 9.

**20. Apparatus**

20.1 All items of 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 2-propanol.

21.2 *Chloroform* ($CHCl_3$).

21.3 *Cobalt Solution, Intermediate* (1.0 mL = 100 µg Co)—See 11.2.

21.4 *Cobalt Solution, Standard* (1.0 mL = 1 µg Co)—Dilute 10 mL of cobalt solution, intermediate, and 1 mL of $HNO_3$ (sp gr 1.42) to 1 L with water. This standard is used to prepare working standards at the time of analysis.

21.5 *Cobalt Solution, Stock* (1.0 mL = 1.0 mg Co)—See 11.1.

21.6 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl) (**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 tubing walls can cause a potentially hazardous situation).

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

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

21.9 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid ($HNO_3$) (**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 tubing walls can cause a potentially hazardous situation).

21.10 *Pyrrolidine Dithiocarbamic Acid-Chloroform Reagent*—Add 36 mL of pyrrolidine to 1 L of $CHCl_3$. Cool the solution and add 30 mL of $CS_2$ in small portions swirling between additions. Dilute to 2 L with $CHCl_3$. 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 flammable. Prepare and use in a well-ventilated hood. Avoid inhalation and direct contact.)

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

21.12 *Materials*—See 11.6 and 11.7.

## 22. Standardization

22.1 Prepare 100 mL each of a blank and sufficient standards containing from 0.0 to 100 µg of cobalt from the cobalt standard solution (see 21.4) by making appropriate dilutions with water. Prepare standards immediately prior to use.

22.2 When determining total recoverable cobalt use 125-mL beakers or flasks. Add 0.5 mL of $HNO_3$ (sp gr 1.42) and proceed as directed in 23.2 to 23.15.

22.3 Construct an analytical curve by plotting the absorbances of standards versus micrograms of cobalt. 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 µg of cobalt (100-mL maximum) into a 125-mL beaker or flask and adjust the volume to 100 mL with water.

NOTE 8—If only dissolved cobalt is to be determined measure a volume of filtered and acidified sample containing less than 100 µg of cobalt (100-mL maximum) into a 250-mL separatory funnel, and proceed from 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 in a well-ventilated hood until the volume has been reduced to 15 to 20 mL, making certain that the samples do not boil.

NOTE 9—When analyzing brine samples and samples containing appreciable amounts 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-texture, acid-washed, ashless paper, into 250-mL separatory funnels. Wash the filter paper two or three times with water and adjust the volume to approximately 100 mL.

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

23.6 Adjust the pH by the 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 10—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 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 $CHCl_3$ phase into a 100-mL beaker.

23.9 Repeat the extraction with 10 mL of $CHCl_3$ and drain the $CHCl_3$ layer into the same beaker.

NOTE 11—If color still remains in the $CHCl_3$ extract, reextract the aqueous phase until the $CHCl_3$ 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 from heat and allow residual solvent to evaporate without further heating. (**Warning**—Perform this procedure in a well-ventilated hood.)

23.11 Hold the beaker at a 45° angle, and slowly add dropwise 2 mL of nitric acid (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 a low heat 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 12—If a precipitate appears when the HCl (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.

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

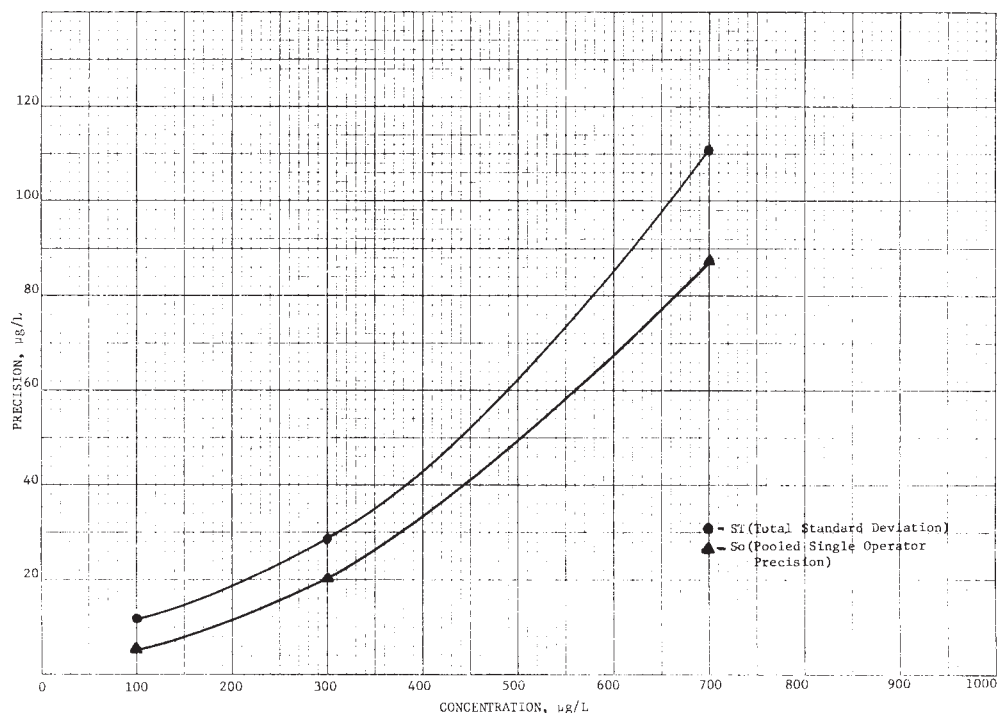23.15 Aspirate each sample and record the scale reading or concentration at 240.7 nm.

**FIG. 3 Precision for Cobalt in Reagent Water, Type II by Atomic Absorption Chelation-Extraction**

## 24. Calculation

24.1 Determine the weight of cobalt in each sample by referring to 22.3. Calculate the concentration of cobalt in micrograms per litre using Eq 2:

$$\text{Cobalt, } \mu g/L = (1000/A) \times B \qquad (2)$$

where:

$A$ = volume of original sample, mL, and
$B$ = weight of cobalt in sample, $\mu$ g.

## 25. Precision and Bias [6]

25.1 The single-operator and overall precision of this test method within its designated range for five laboratories, which include a total of six operators (at 100, 300, and 700 µg/L) analyzing each sample on three different days varies with the quantity being tested in accordance with Fig. 3 and Fig. 4.

25.2 Recoveries of known amounts of cobalt in a series of prepared standards for the same laboratories were as shown in Table 2.

25.3 The waters used in evaluations were reagent water, artificial seawater, river water, tap water, and a synthetic brine. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

25.4 Precision and bias of this test method conform to Practice D 2777 – 77, which was in place at the time of collaborative testing. Under the allowances made in 1.5 of Practice D 2777 – 86, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D–19 test methods.

25.5 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.

## 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 cobalt.

26.2 *Calibration and Calibration Verification*

26.2.1 Analyze at least three working standards containing concentrations of cobalt 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 cobalt. The matrix and chemistry of
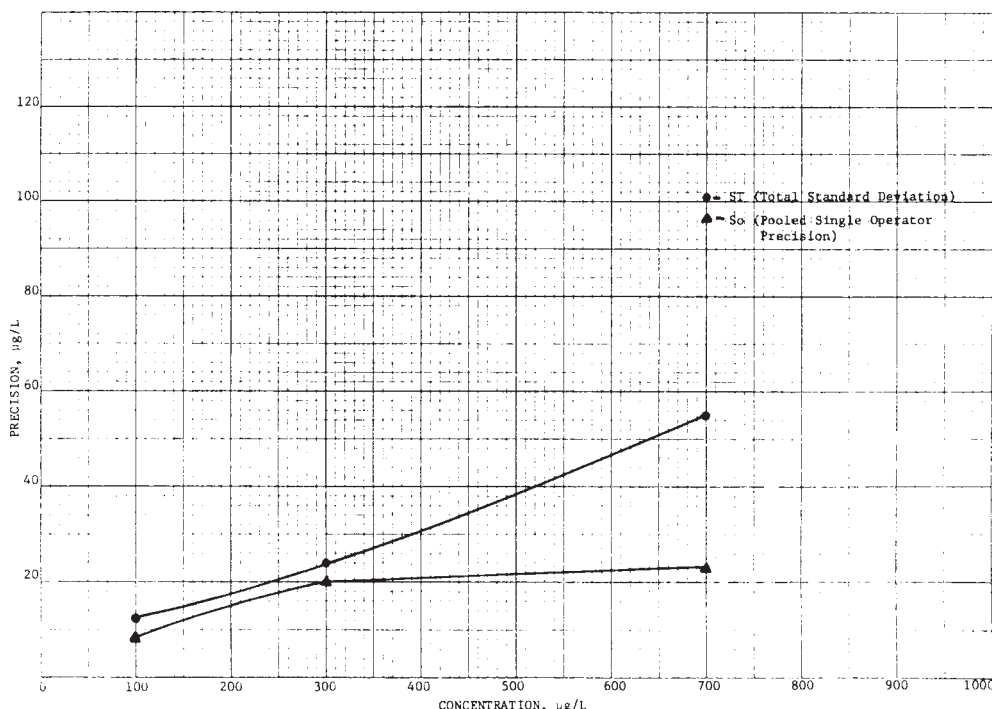
**FIG. 4 Precision for Cobalt in Water of Choice by Atomic Absorption Chelation-Extraction**

**TABLE 2 Recoveries of Known Amounts of Cobalt Atomic Absorption, Chelation-Extraction**

| | Amount Added, µg/L | Amount Found, µg/L | Bias, % | Statistically Significant (95 % Confidence Level) |
|---|---|---|---|---|
| Reagent water, Type II | 100 | 102 | +2.0 | no |
| | 300 | 297 | −1.0 | no |
| | 700 | 633 | −9.6 | no |
| Water of choice | 100 | 104 | +4.0 | no |
| | 300 | 295 | −1.7 | no |
| | 700 | 708 | +1.1 | no |

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 cobalt with each batch or 10 samples. If large numbers of samples are analyzed in the batch, analyze the LCS after every 10 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 ±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 cobalt found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of cobalt 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 cobalt and taking it through the analytical method.

26.6.2 The spike concentration plus the background concentration of cobalt 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:

$$P = [A(V_s + V) - BV_s] / CV \qquad (3)$$

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 13—Acceptable spike recoveries are dependent on the concentration 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 cobalt in most waters and wastewaters.

27.2 This test method is applicable in the range from 5 to 100 µg/L of cobalt. 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.

27.3 This test method has been used successfully with reagent water, lake water, river water, well water, filtered tap water, condensate from a medium Btu coal gasification process, and effluent from a wood treatment plant. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

27.4 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 Cobalt 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. Since the graphite furnace uses the sample much more efficiently than flame atomization, the detection of low concentrations of elements in small sample volumes is possible. Finally, 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 cobalt is determined on a filtered sample with no pretreatment.

28.3 Total recoverable cobalt 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.

### 30. Apparatus

30.1 *Atomic-Absorption Spectrophotometer*, for use at 240.7 nm with background correction.

NOTE 14—A wavelength other than 240.7 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 15—The manufacturer's instructions should be followed for all instrumental parameters.

30.2 *Cobalt Light Source*—Cobalt 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. Standard graphite tubes are preferred unless extreme sensitivity is required. In this instance and to eliminate the possible formation of carbides, pyrolytically coated graphite tubes are recommended.

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* should be used, if available.

## 31. Reagents and Materials

31.1 *Cobalt Solution, Stock* (1 mL = 1 mg Co)—See 11.1.

31.2 *Cobalt Solution, Intermediate* (1 mL = 10 µg Co)— Dilute 10 mL of cobalt solution, stock (see 11.1) with 1 mL of $HNO_3$ (sp gr 1.42) to 1 L with water.

31.3 *Cobalt Solution, Standard* (1 mL = 0.10 µg Co)— Dilute 10 mL of cobalt solution, intermediate (see 31.3) with 1 mL of $HNO_3$ (sp gr 1.42) to 1 L with water. This standard is used to prepare working standards at the time of the analysis.

31.4 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid ($HNO_3$) (see Note 4).

31.5 *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 in accordance with manufacturer's specifications. Follow the general instructions as provided in Practice D 3919.

## 33. Procedure

33.1 Clean all glassware to be used for preparation of standard solutions or in the digestion step, or both, by soaking the glassware overnight in (1 + 1) $HNO_3$.

33.2 Measure 100.0 mL of each standard and well-mixed sample into a 125-mL beaker or flask.

33.3 For total recoverable cobalt, add 5 mL of $HNO_3$ (sp gr 1.42) to each standard and sample and proceed as directed in 33.4 through 33.6. If only dissolved cobalt is to be determined, filter the unacidified sample through a 0.45-µm membrane filter, acidify, and proceed to 33.6.

33.4 Heat 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 9).

33.5 Cool and filter the sample through a suitable filter such as fine-texture, acid-washed, ashless paper, into a 100-mL volumetric flask. Wash the filter paper two or three times with water and bring to volume.

NOTE 16—If suspended material is not present, this filtration may be omitted.

33.6 Inject a measured aliquot of 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 cobalt in each sample by referring to Practice D 3919.

## 35. Precision and Bias [7]

35.1 The precision of this test method was tested by 12 laboratories in reagent water, lake water, river water, well

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[7] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D19–1109.

water, filtered tap water, condensate from a U-gas process, and effluent from a wood treatment plant. 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 3.

**TABLE 3 Determination of Bias and Overall Precision, Atomic Absorption Graphite Furnace**

| | Amount Added, µg/L | Amount Found, µg/L | $S_T$ | ±Bias | ±%Bias | Statistically Significant |
|---|---|---|---|---|---|---|
| Reagent Water | 40.0 | 42.10 | 6.72 | +2.10 | +5.2 | no |
| | 8.0 | 8.28 | 1.26 | +0.28 | +3.5 | no |
| | 20.0 | 20.90 | 2.38 | +0.90 | +4.5 | no |
| Water of choice | 40.0 | 39.30 | 4.82 | −0.70 | −1.75 | no |
| | 8.0 | 8.03 | 0.74 | +0.03 | +0.38 | no |
| | 20.0 | 20.10 | 2.15 | +0.10 | +0.50 | no |

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 the test method in a particular matrix.

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 cobalt.

36.2 *Calibration and Calibration Verification*

36.2.1 Analyze at least three working standards containing concentrations of cobalt 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 ±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 cobalt. 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 cobalt with each batch or 10 samples. If large numbers of samples are analyzed in the batch, analyze the LCS after every 10 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 ±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 cobalt found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of cobalt 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 cobalt and taking it through the analytical method.

36.6.2 The spike concentration plus the background concentration of cobalt 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:

$$P = [A(V_s + V) – BV_s] / CV \qquad (4)$$

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 17—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; cobalt; graphite furnace; water

## SUMMARY OF CHANGES

Committee D19 has identified the location of selected changes to this standard since the last issue (D3558–94 (1998)) that may impact the use of this standard.

*(1)* Sections 15.4, 25.4, and 35.3 were added.

*(2)* The QC sections 16, 26, and 36 were added to the test method.

*(3)* All sections after 15 were renumbered.