Designation: D 3558 – 94 (Reapproved 1998)

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 15
Test Method B—Atomic Absorption, Chelation-Extraction	10 to 1000 µg/L	16 to 24
Test Method C—Atomic Absorption, Graphite Furnace	5 to 100 µg/L	25 to 33

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 Note 3, Note 5, Note 8, and Note 13.

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 Total 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 D–19 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]

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 Reagents of the American Chemical Society where such

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

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[2] Platte, J. A., and March, V. M., "A New Tool for the Water Chemist," *Industrial Water Engineering*, May 1965.

[3] *Annual Book of ASTM Standards*, Vol 11.01.

specifications are available.[4] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Unless otherwise indicated, 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. **Caution**—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).

NOTE 5—**Warning:** "Purified" grade acetylene containing a special

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[4] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

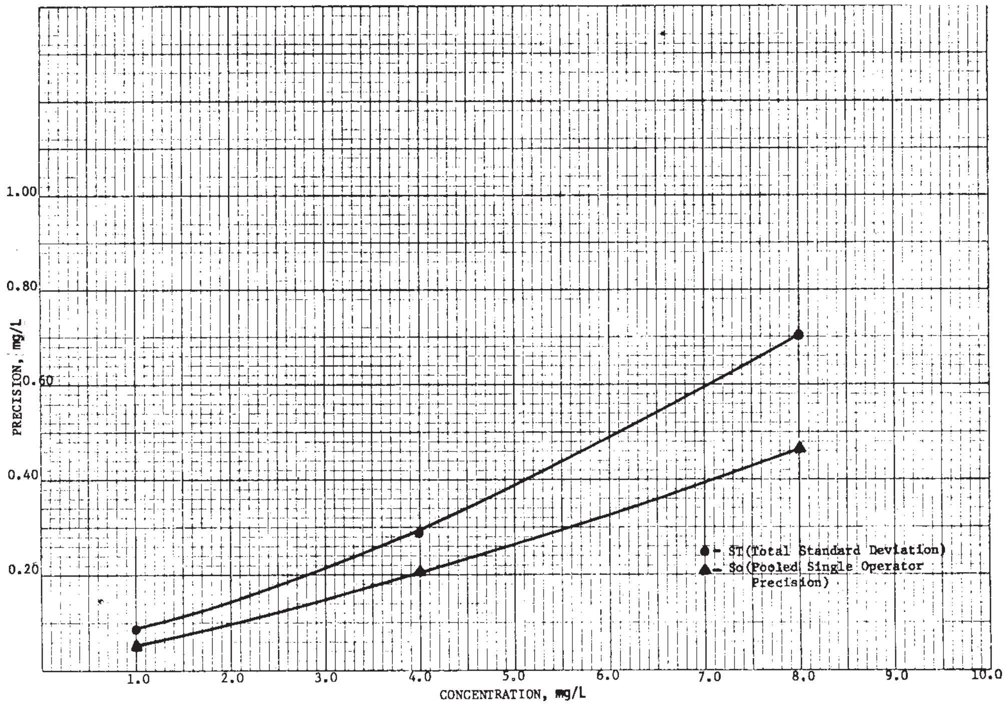

FIG. 1 Precision for Cobalt in Reagent Water, Type II by Direct Atomic Absorption

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.

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 6—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 7—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 [5]

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.

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[5] Supporting data for these test methods have been filed at ASTM Headquarters. Request RR:D-19-1032.

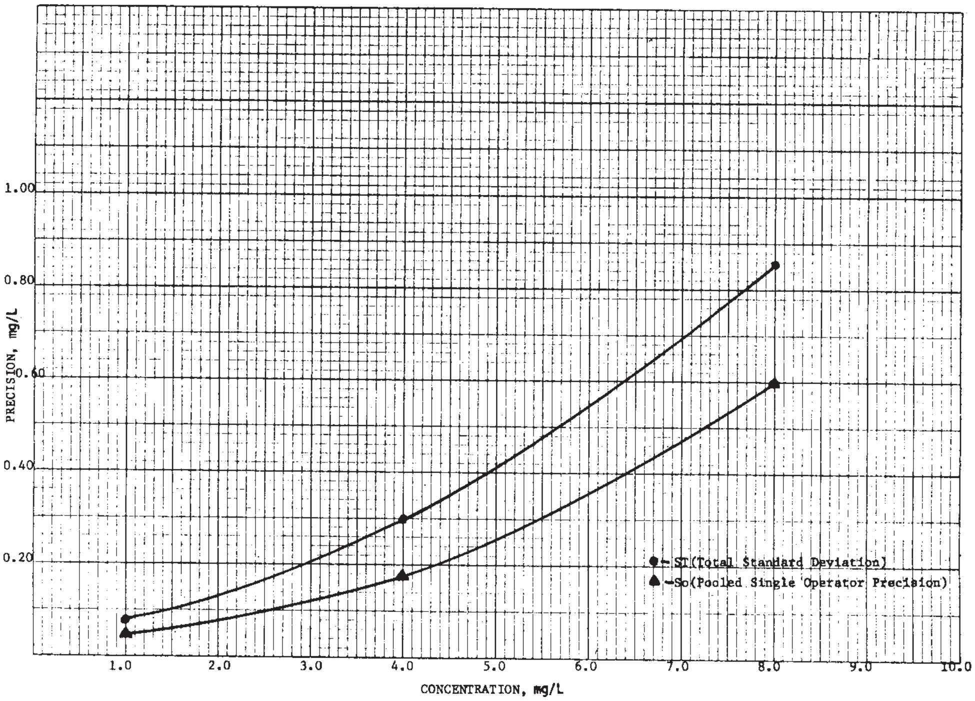

FIG. 2 Precision for Cobalt in Water of Choice by Direct Atomic Absorption

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

TEST METHOD B—ATOMIC ABSORPTION, CHELATION-EXTRACTION

16. Scope

16.1 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.

16.2 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.

17. Summary of Test Method

17.1 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).

18. Interferences

18.1 See Section 9.

19. Apparatus

19.1 All items of apparatus described in Section 10 are required.

20. Reagents and Materials

20.1 *Bromphenol Blue Indicator Solution* (1 g/L)—Dissolve 0.1 g of bromphenol blue in 100 mL of 50 % ethanol or 2-propanol.

20.2 *Chloroform* ($CHCl_3$).

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

20.4 *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.

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

20.6 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl) (see Note 3).

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