



Designation: ~~D 511-03~~ Designation: D 511 – 08

Standard Test Methods for Calcium and Magnesium In Water¹

This standard is issued under the fixed designation D 511; 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 calcium and magnesium in water by complexometric titration and atomic absorption spectrometric procedures. Two test methods are included, as follows:

Test Method A—Complexometric Titration	Sections 7 to 14
Test Method B—Atomic Absorption Spectrometric	15 to 23

1.2

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

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. Specific hazard statements are given in 12.2.6 and 20.6.

2. Referenced Documents

2.1 ASTM Standards:²

D 1129 Terminology Relating to Water

D 1193 Specification for Reagent Water

D 2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water

D 3370 Practices for Sampling Water from Closed Conduits

D 4691 Practice for Measuring Elements in Water by Flame Atomic Absorption Spectrophotometry

D 4841 Practice for Estimation of Holding Times~~Time~~ for Water Samples Containing Organic and Inorganic Constituents

D 5810 Guide for Spiking ~~Into~~ Aqueous Samples

D 5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis

3. Terminology

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

4. Significance and Use

4.1 Calcium and magnesium salts in water are the primary components of water hardness which can cause pipe or tube scaling.

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.³ 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

¹ 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 1937. Last previous edition approved in 1998 as D511-93 (1998).

Current edition approved Oct. 1, 2008. Published November 2008. Originally approved in 1937. Last previous edition approved in 2003 as D 511 – 03.

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards*, Vol 11.01, volume information, refer to the standard's Document Summary page on the ASTM website.

³ *Annual Book of ASTM Standards*, Vol 11.02, 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 *Annual 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.

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

Specification D 1193, Type 1, II, or III water. Type I is preferred and more commonly used. Type II water was specified at the time of round-robin testing of these test methods.

NOTE 1—The user must ensure the type of reagent water is sufficiently free of interferences. The water should be analyzed using this test method.

6. Sampling

6.1 Collect the sample in accordance with Practices D 3370.

6.2 If total recoverable calcium and magnesium concentrations are being determined, acidify the water sample with HNO₃ (sp gr 1.42) to a pH of 2 or less immediately at the time of collection; normally about 2 mL/L are required. The holding time for the samples may be calculated in accordance with Practice D 4841.

6.3 If dissolved calcium and magnesium concentrations are being determined, filter the samples through a 0.45- μ m membrane filter and acidify with HNO₃ (sp gr 1.42) to a pH of 2 or less immediately at time of collection; normally about 2 mL/L are required.

6.4 A number of sources of calcium contamination have been encountered in laboratories. Among the most common are plastic ware, paper towels, and dust. Rinsing plastic ware with sample prior to use, avoiding contact of apparatus with paper towels, and keeping exposure to the air to a minimum will limit the possibility of contamination.

TEST METHOD A—COMPLEXOMETRIC TITRATION

7. Scope

7.1 This test method is applicable to most waters in a range from 1 to 1000 mg/L of calcium plus magnesium expressed as calcium, but may fail in the analysis of highly colored waters, brines, or waters that contain excessive amounts of metals. The upper and lower limits may be extended by either dilution or use of micro apparatus.

7.2 Data are not available to determine which matrices were used to obtain the precision and bias data, and it is the responsibility of the analyst to determine the acceptability of this test method for the matrix being analyzed.

8. Summary of Test Method

8.1 EDTA (ethylenediamine tetraacetic acid or its salts) is added to a sample containing calcium and magnesium ions after the pH of the solution is adjusted to 10 for the determination of calcium and magnesium or from pH 12 to 13 for the determination of calcium alone. The EDTA initially complexes the calcium and then the magnesium. The end point is observed by the use of a suitable indicator. At a pH of 12 to 13 magnesium is precipitated. Magnesium is determined by the difference between an aliquot titrated at pH 10 and one titrated at pH 12 to 13.

9. Interferences

9.1 EDTA reacts with iron, manganese, copper, zinc, lead, cobalt, nickel, barium, strontium, calcium, magnesium, and several other metals. The interference of heavy metals is minimized by the addition of hydroxylamine and cyanide, which reduce or complex the metals, or both. Metal concentrations as high as 5 mg/L of iron, 10 mg/L of manganese, 10 mg/L of copper, 10 mg/L of zinc, and 10 mg/L of lead can be tolerated when hydroxylamine and cyanide are added.

9.2 In the titration of calcium plus magnesium, the higher oxidation states of manganese above Mn⁺² react rapidly with the indicator to form discolored oxidation products. Hydroxylamine hydrochloride reagent is used to reduce manganese to the divalent state. The divalent manganese interference can be eliminated by addition of one or two small crystals of potassium ferrocyanide.

9.2.1 Orthophosphate and sulfate ions interfere at concentrations in excess of 500 and 10 000 mg/L, respectively.

9.2.2 In the presence of aluminum concentrations in excess of 10 mg/L, the blue color that indicates that the end point has been reached will appear and then, on short standing, will revert to red. The reversion should not be confused with the gradual change that normally takes place in the titrated sample several minutes after the titration has been completed.

9.3 In the titration of calcium, ammonium purpurate reacts with strontium but not with magnesium or barium. However, the end point in the presence of strontium is sluggish, and the titration is not strictly stoichiometric. Barium does not titrate as calcium, but affects the indicator in some unknown way so that no end point, or at best a poor end point, is obtained. Barium can be removed by prior precipitation with sulfuric acid, but care must be exercised to prevent precipitation of calcium. Orthophosphate will precipitate calcium at the pH of the test.

9.4 A possible interference from the commonly used polyphosphates, organic phosphonates, and EDTA/NTA compounds in water treatment should be recognized.

10. Apparatus

10.1 *Titration Assembly*—Some analysts prefer to use conventional lighting and hand stirring. Others report better results by using a visual-titration assembly consisting of a motor-driven stirrer, 25-mL burette, white-porcelain-base burette holder, and shaded incandescent lamp. The sample beaker is placed near the front of the porcelain base and the reaction is viewed diagonally downward through the side of the beaker and against the white background. Illumination is from behind the beaker. The capacity of the burette, type lighting, and background color may be varied depending on the ionic concentrations normally encountered and the indicator chosen.

10.2 *pH Meter*, with expanded mV scale.

11. Reagents

11.1 *Buffer Solution, Ammonium Chloride-Ammonium Hydroxide*—Dissolve 67.6 g of ammonium chloride (NH_4Cl) in 200 mL of water. Add 570 mL of concentrated ammonium hydroxide (NH_4OH , sp gr 0.900). Add 5.00 g of magnesium salt of EDTA and dilute to 1000 mL. Store in a tightly stoppered plastic bottle to prevent the loss of ammonia. Discard the solution when 1 mL added to a neutralized sample fails to produce a pH of 10.0 ± 0.1 at the titration end point. To attain highest accuracy, adjust the magnesium level to exact equivalence through the appropriate addition of a small amount of either disodium EDTA or magnesium sulfate (MgSO_4).

11.2 *Calcium Indicator Solution:*

11.2.1 *Ammonium Purpurate*—Mix thoroughly 1.0 g of ammonium purpurate with 200 g of sucrose. Place in a bottle provided with a dispensing spoon of 0.2-g capacity.

11.2.2 *Fluorescein Methylene Iminodiacetic Acid*⁴—Grind 0.2 g of fluorescein methylene iminodiacetic acid and 0.12 g of thymolphthalein with 20 g of potassium chloride to 40 to 50 mesh size. Place in a bottle provided with a dispensing spoon of 0.2-g capacity.

11.3 *Calcium Solution, Standard (1.00 mL = 0.400 mg calcium)*—Suspend 1.000 g of calcium carbonate (CaCO_3), dried at 180°C for 1.0 h before weighing, in approximately 600 mL of water and dissolve cautiously with a minimum of dilute HCl. Dilute to 1000 mL with water in a volumetric flask.

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11.3.1 Alternatively, certified calcium stock solutions are commercially available through chemical supply vendors and may be used.

11.4 *Chrome Black T Solution (4.0 g/L)*—Dissolve 0.4 g of Chrome Black T in 100 mL of water. This solution has a shelf life of approximately 1 week. Alternatively, a dry powder mixture composed of 0.5 g of dye and 100 g of powdered sodium chloride may be used. Store this in a dark-colored bottle provided with a dispensing spoon of approximately 0.2-g capacity. The shelf life is at least 1 year.

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NOTE 2—Chrome Black T is also known as Eriochrome Black T.

11.5 *EDTA Solution, Standard (0.01 M, 1 mL = 0.401 mg calcium or 0.243 mg manganese)*—Dissolve 3.72 g of Na_2EDTA dihydrate, which has been dried overnight over H_2SO_4 in a desiccator, in water (or at 80°C . for 1 hour) and dilute to 1000 mL in a volumetric flask. The reagent is stable for several weeks. Check the titer of the reagent by titrating 25.00 mL of CaCO_3 standard solution as described in the procedure for sample analysis.

11.6 *Hydroxylamine Hydrochloride Solution (30 g/L)*—Dissolve 30 g of hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) in water and dilute to 1000 mL.

11.7 *Potassium Ferrocyanide*—($\text{K}_4\text{Fe}(\text{CN})_6\cdot 3\text{H}_2\text{O}$).

11.8 *Sodium Cyanide Solution (25 g/L)*—Dissolve 25 g of sodium cyanide (NaCN) in water and dilute to 1000 mL. (**Warning—Warning:** Sodium cyanide is a deadly poison. Do not add NaCN to any acid solution or acidify any solution containing it. Use this reagent in a fume hood.)

11.9 *Sodium Hydroxide Solution (80 g/L) (80 g/L or 2 M)*—Dissolve 80 g of sodium hydroxide (NaOH) in 800 mL of water. Cool and dilute to 1000 mL.

11.9.1 Alternatively, a commercially prepared solution of sodium hydroxide is available through chemical supply vendors and may be used.

12. Procedure

12.1 *Calcium Plus Magnesium:*

12.1.1 Measure 100.0 mL of a well-mixed acidified sample (see 6.2) into a 125-mL beaker or flask.

NOTE 2—If only dissolved calcium plus magnesium is to be determined, omit 12.1.1 through 12.1.4 and proceed to 12.1.5.

12.1.2 Add 5 mL of hydrochloric acid (HCl , sp gr 1.19) to each sample.

12.1.3 Heat the samples on a steambath or hot plate until the volume has been reduced to 15 to 20 mL, making certain that the samples do not boil.

NOTE 3—For samples with high levels of dissolved or suspended matter, the amount of reduction in volume is left to the discretion of the analyst.

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

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.

⁴ Calcein, W., Fluorescein Complexon, and Fluorexon, supplied by various commercial firms, have been found satisfactory for this purpose.

12.1.5 ~~Pipette~~ Measure 50 mL of the filtered sample (50.00-mL maximum) into a 150-mL beaker and adjust the volume to approximately 50 mL. Adjust the pH to 7 to 10 by the dropwise addition of ammonium hydroxide (NH₄OH, sp gr 0.900).

~~NOTE 4~~ For ~~5~~ For analysis of brines an appropriate aliquot size often can be determined from knowledge of the specific gravity, for example:

1.000 to 1.025, use 25 mL
 1.025 to 1.050, use 10 mL
 1.050 to 1.090, use 5 mL
 1.090 to 1.120, use 1 mL
 1.120 to 1.180, use 0.1 mL

12.1.6 Insert the beaker in the titration assembly and start the stirrer.

12.1.7 Add 1 mL of NH₂OH·HCl solution (11.6).

12.1.8 Add 1 mL of buffer solution (11.1). Measure the pH and verify that it falls in the pH range from 10.0 + 0.1. Adjust by the dropwise addition of ammonium hydroxide.

12.1.9 Add 2 mL of NaCN solution (~~Warning—11.8~~) **Warning:** Sodium cyanide is a deadly poison. Do not add NaCN to any acid solution or acidify any solution containing it. Use this reagent in a fume ~~hood~~ hood.

12.1.10 If manganese is present, add one or two small crystals K₄Fe(CN)₆·3H₂O (11.7).

12.1.11 Add 4 to 5 drops of Chrome Black T indicator solution (11.4). If powdered indicator is used add approximately 0.2 g.

12.1.12 Titrate with standard EDTA solution (11.5) until blue or purple swirls begin to show. The end point is reached when all traces of red and purple have disappeared and the solution is ~~clear~~ pure blue in color. The titration should be completed within 5 min of the buffer addition. If more than 15 mL of titrant is required, take a smaller sample aliquot and repeat the test.

12.1.13 Record the volume of EDTA solution required to titrate calcium plus magnesium.

12.1.14 Determine a reagent blank correction by similarly titrating 50 mL of water including all added reagents.

12.2 *Calcium:*

~~12.2.1 Refill the burette with EDTA standard solution.~~

12.2.1 Refill the burette with EDTA standard solution (11.5).

12.2.2 Pipette another aliquot of the same sample (50.00 mL maximum) into a 150-mL beaker and adjust the volume to approximately 50 mL (see ~~Note 4~~ Note 5).

12.2.3 Insert the beaker in the titration assembly and start the stirrer.

12.2.4 Add 1 mL of NH₂OH·HCl.

~~12.2.5 Add 1 mL of NaOH solution. The pH should range from 12 to 13. OH·HCl (11.6).~~

12.2.5 Add 1 mL of NaOH solution (11.9). The pH should range from 12 to 13.

12.2.6 Add 1 mL of NaCN (~~Warning—11.8~~) **Warning:** Sodium cyanide is a deadly poison. Do not add NaCN to any acid solution or acidify any solution containing it. Use this reagent in a fume ~~hood~~ hood.

12.2.7 Add 0.2 g of calcium indicator solution (11.2) and proceed immediately with the titration.

12.2.8 Titrate with standard EDTA solution (11.5) to the appropriate end point. If ammonium purpurate is used, the end point will be indicated by color change from ~~salmon~~ orange pink to ~~orchid~~ pale pinkish purple. If fluorescein methylene iminodiacetic acid is used, the end point will be indicated by a color change from deep green to purple. The titration should be completed within 5 min of the addition of NaOH solution. If more than 15 mL of titrant is required, take a smaller sample aliquot and repeat the test.

12.2.9 Record the volume of EDTA solution required to titrate the calcium.

12.2.10 Determine a reagent blank correction by similarly titrating 50 mL of water including all added reagents.

13. Calculation

13.1 Calculate the concentration of calcium and magnesium in milligrams per litre using Eq 1 and Eq 2:

$$\text{Calcium, mg/L} = (A \times B/D) \times 40\ 100 \quad (1)$$

$$\text{Magnesium, mg/L} = ((C \times B/E) - (A \times B/D)) \times 24\ 300 \quad (2)$$

where:

A = EDTA standard solution required to titrate calcium in 12.2.9 minus the blank correction determined in 12.2.10, mL,

B = molarity of EDTA standard solution,

C = EDTA standard solution required to titrate calcium plus magnesium in 12.1.13 minus the blank correction determined in 12.1.14, mL,

D = sample taken in 12.2.2, mL, and

E = sample taken in 12.1.5, mL.

13.2 If the concentration of strontium is determined to be significant (see Sections 9.1 and 9.3), make a correction for strontium concentration using Eq 3:

$$\begin{aligned} \text{Corrected mg/L calcium} &= \text{mg/L calcium} \\ &- (\text{mg/L strontium} \times 0.46) \end{aligned} \quad (3)$$

13.3 Results for calcium and magnesium may be represented as CaCO₃ using Eq 4 and Eq 5:

$$\text{Calcium (as CaCO}_3\text{), mg/L} = \text{mg/L Ca} \times 2.50 \quad (4)$$

$$\text{Magnesium (as CaCO}_3\text{), mg/L} = \text{mg/L Mg} \times 4.12 \quad (5)$$

14. Precision and Bias⁵

14.1 Data are not available to determine which matrices were used to obtain precision and bias data.

14.2 The precision of this test method for calcium, ranging in calcium concentration between 13 and 88 mg/L, may be expressed using Eq 6 and Eq 7:

$$S_T = 0.006 X + 0.62 \quad (6)$$

$$S_O = 0.006 X + 0.51 \quad (7)$$

where:

S_T = overall precision,

S_O = single-operator precision, and

X = determined concentration of calcium, mg/L.

14.3 *Bias*—Recoveries of known amounts of calcium using this test method were as follows:

Amount Added, mg/L	Amount Found, mg/L	Bias, %	Statistically Significant, 95 % Confidence Level
13.3	13.5	+1.5	no
41.8	43.0	+2.9	yes
84.6	87.7	+3.7	yes

14.4 This information was derived from round-robin testing in which four laboratories, including eight operators, participated. No data were rejected. Four sample levels were run on each of three days, but one level was rejected as having grossly deteriorated in shipment. The method of “least squares” was used to determine the precision statements.

14.5 The precision of this test method for magnesium ranging in magnesium concentration from between 2.5 and 36 mg/L may be expressed using Eq 8 and Eq 9:

$$S_T = 0.017 X + 0.85 \quad (8)$$

$$S_O = 0.002 X + 0.70 \quad (9)$$

where:

S_T = overall precision,

S_O = single-operator precision, and

X = determined concentration of magnesium, mg/L.

14.6 *Bias*—Recoveries of known amounts of magnesium using this test method were as follows:

Amount Added, mg/L	Amount Found, mg/L	Bias, %	Statistically Significant, 95 % Confidence Level
2.38	2.54	+6.7	no
14.7	15.0	+2.0	no
22.2	21.8	-1.8	no
35.9	36.1	+0.6	no

14.7 This information was derived from round-robin testing in which four laboratories, including eight operators, participated. No data were rejected. Four sample levels were run on each of three days. The method of “least squares” was used to determine the precision statements.

14.8 The single-operator precision for calcium determined for synthetic sodium chloride brines having the composition listed in Table 1 is as follows:

$$S_O = 76$$

For magnesium, it is:

$$S_O = 51$$

14.9 These data may not apply to waters of other matrices.

14.10 Four independent laboratories participated in the round-robin study.

⁶ Calcein, W., Fluorescein Complexon, and Fluorexon, supplied by various commercial firms, have been found satisfactory for this purpose.

⁵ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D19-1027.

TABLE 1 Composition of Synthetic Sodium Chloride

Component	Brine Test Solutions (All Concentrations, mg/L)			
	30 000	50 000	100 000	150 000
NaCl	30 000	50 000	100 000	150 000
Ba	1 000	1 000	1 000	1 000
Sr	1 000	1 000	1 000	1 000
Mg	1 200	5 000	7 000	10 000
Ca	2 500	12 000	15 000	25 000

14.11 This section of 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~~, D 2777 – 06, these precision and bias data do meet existing requirements of interlaboratory studies of Committee D19 test methods.

15. Quality Control

15.1 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 calcium and magnesium in water.

15.2 Calibration and Calibration Verification

15.2.1 Analyze at least three working standards containing concentrations of calcium and magnesium in water that bracket the expected sample concentration, prior to analysis of samples, to calibrate the instrument. The calibration correlation coefficient should 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.

15.2.2 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.

15.2.3 If calibration cannot be verified, recalibrate the instrument.

15.3 Initial Demonstration of Laboratory Capability

15.3.1 If a laboratory has not performed the test before, or if there has been a major change in the measurement system, for example, a new analyst, new instrument, and so forth, a precision and bias study must be performed to demonstrate laboratory capability.

15.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material containing a mid-range concentration of calcium and magnesium in water. 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.

15.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in Table 2. If a concentration other than the recommended concentration is used, refer to Practice D 5847 for information on applying the F test and t test in evaluating the acceptability of the mean and standard deviation.

15.4 Laboratory Control Sample (LCS)

15.4.1 To ensure that the test method is in control, analyze an LCS containing a known concentration of calcium and magnesium in water 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 should fall within $\pm 15\%$ of the known concentration.

15.4.2 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.

15.5 Method Blank

15.5.1 Analyze a reagent water test blank with each batch. The concentration of calcium and magnesium in water found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of calcium and magnesium in water 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.

15.6 Matrix Spike (MS)

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

15.6.2 The spike concentration plus the background concentration of calcium and magnesium in water must not exceed the high calibration standard. The spike must produce a concentration in the spiked sample that is two to five times the analyte concentration in the unspiked sample, or 10 to 50 times the detection limit of the test method, whichever is greater.

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

$$P = \frac{100 [A(V_s + V) - BV_s]}{CV} \quad (10)$$