Designation: D7318 − 13

Standard Test Method for
Existent Inorganic Sulfate in Ethanol by Potentiometric Titration[1]

This standard is issued under the fixed designation D7318; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 This test method covers a potentiometric titration procedure for determining the existent inorganic sulfate content of hydrous, anhydrous ethanol, and anhydrous denatured ethanol, which is added as a blending agent with spark ignition fuels. It is intended for the analysis of denatured ethanol samples containing between 1.0–20 mg/kg existent inorganic sulfate.

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.* Material Safety Data Sheets are available for reagents and materials. Review them for hazards prior to usage.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water
D4052 Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter
D4057 Practice for Manual Sampling of Petroleum and Petroleum Products
D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products
D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

3. Terminology

3.1 *Definitions:*

3.1.1 *existent inorganic sulfate, n*—inorganic sulfate species actually present in the sample at the time of analysis with no oxidation treatment.

3.1.1.1 *Discussion*—Specifically in this test method, inorganic sulfate is present as sulfate in ethanol.

3.1.2 *inorganic sulfate, n*—sulfate (SO_4^{-2}) species present as sulfuric acid, ionic salts of this acid, or mixtures of these.

4. Summary of Test Method

4.1 An ethanol sample containing inorganic sulfate is titrated in ethanolic medium with a standard lead nitrate solution. Lead sulfate precipitate is formed during the titration. Perchloric acid is added to remove possible interference from carbonate. The endpoint is signaled by an increase in lead ion activity, as measured by a lead–selective electrode.

5. Significance and Use

5.1 Ethanol is used as a blending agent added to gasoline. Sulfates are indicated in filter plugging deposits and fuel injector deposits. When fuel ethanol is burned, sulfates may contribute to sulfuric acid emissions. Ethanol acceptability for use depends on the sulfate content. Sulfate content, as measured by this test method, can be used as one measure of determination of the acceptability of ethanol for automotive spark-ignition engine fuel use.

6. Apparatus

6.1 *Potentiometric Titration Assembly*—A titration assembly consisting of an automatic titrator fitted with a lead ion-selective electrode, a double-junction reference electrode, buret, and stirring is used. Stirring may be accomplished by means of magnetic or propeller type stirrer mechanisms. The buret size should ideally be 10 or 20 mL.

6.2 *Reference Electrode*—A double junction reference electrode with the inner electrode composed of silver/silver chloride with a potassium chloride solution as internal electrolyte. The external solution is composed of 1 M lithium chloride in ethanol. This configuration is used to prevent silver ion, a lead electrode poison, from leaching into the analyte solution during titration. Preferred electrolytes for use in double junction electrodes may vary with the manufacturer; use the manufacturer's recommended electrolytes for the application. Other

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[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

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

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

types of reference electrodes may be considered with some caveats (for example, single junction, combination, or glassy carbon), but the data presented in this test method were generated using exclusively a double junction electrode, which is the best choice for this determination.

6.3 *Lead Electrode*—A lead sulfide–based crystalline sensor type lead ion selective electrode (ISE) is used.

6.4 *Drying Oven*—A drying oven for drying sodium sulfate at 110°C is required.

6.5 *Pipets or Volumetric Transferring Devices*—Class A glass pipets or their equivalent.

6.6 *Polishing Material*—Lead sulfide based crystalline sensor electrodes require polishing to remove oxidation products. These materials are supplied with the electrode from the manufacturer.

6.7 *pH Test Strips*—Test strips in the range of pH 1 to pH 7.

6.8 *Titration Vessels*—Standard glass beakers or titration vessels supplied with titration equipment.

7. Reagents and Materials

7.1 *Lead Nitrate*—Reagent grade, 99% minimum purity. (**Warning—**Poison, harmful by inhalation and if ingested. Avoid contact with the skin.) Dispose of this material in accordance with accepted local requirements.

7.2 *Sodium Sulfate*—Anhydrous, reagent grade, 99% minimum purity. (**Warning—**Do not ingest. Avoid unnecessary exposure.)

7.3 *Perchloric Acid 70%*—A.C.S. reagent grade, minimum purity with sulfate concentration <0.001% (m/M). Dispose of this material in accordance with accepted local requirements. It must contain no measurable sulfate. (**Warning—**Corrosive; keep away from skin and eyes. Perchloric acid is a strong oxidizer.)

7.4 *Ethanol*—Denatured with methanol, formula 3A or histological grade ethanol, anhydrous, denatured with ethyl acetate, methyl isobutyl ketone and hydrocarbon naphtha. It must be free of any measurable sulfate. (**Warning—**Flammable, toxic, may be harmful or fatal if ingested or inhaled. Avoid skin contact.)

7.5 *Ethanol*—Absolute, 200 proof, 99.5%, A.C.S. reagent grade.

7.6 *Lithium Chloride*—99+%, A.C.S. reagent grade.

7.7 *Water*—Type III reagent water conforming to Specification D1193.

7.8 *Anhydrous Calcium Sulfate Desiccant.*

8. Preparation of Standard Solutions

8.1 *Lead Nitrate Titrant, 0.0025 M*—Dissolve 0.833 g lead nitrate in 300 mL water. Pour into a 1-L bottle and fill with denatured ethanol and mix well. Standardize in accordance with 10.1.

8.1.1 Alternatively, this solution may be purchased from a commercial vendor, and its exact molarity shall be determined in accordance with 10.1.

8.2 *Aqueous Sulfate Standard, 0.01 M*—Dry 5 g anhydrous sodium sulfate at 110°C for 1 h. Remove it from the oven, and allow it to cool in a desiccator over anhydrous calcium sulfate. Accurately weigh about 0.70 g on an analytical balance to the nearest tenth of a milligram, and place it in a 500-mL volumetric flask. Add Type III water to dissolve the sodium sulfate, then dilute to volume. Calculate the exact concentration in accordance with Eq 1.

$$\frac{G}{(142.02)(0.500)} = \text{Molarity} \tag{1}$$

Molarity = molarity of sulfate standard solution, mol/L,
G = weight in grams of Na_2SO_4, dissolved in 500 mL, and
142.02 = gram molecular weight of Na_2SO_4.

8.3 *Aqueous Sulfate Stock Solution for Standards in Ethanol, 2000 mg/L*—Accurately weigh 2.95 g anhydrous sodium sulfate to the nearest tenth of a milligram and transfer it to a 1-L volumetric flask. (Dried anhydrous sodium sulfate should be stored in a desiccator.) Add Type III water to dissolve the sodium sulfate, and make to volume. Calculate the concentration of sulfate in the solution in accordance with Eq 2.

$$\text{Aqueous Stock Sulfate (mg/L)} = \frac{(\text{g } Na_2SO_4)\,(0.6764)\,(1000 \text{ mg/g})}{1 \text{ L}} \tag{2}$$

g Na_2SO_4 = weight in grams of Na_2SO_4 dissolved in 1 L, and
0.6764 = fraction of sulfate in Na_2SO_4.

8.4 *Sulfate Standards in Ethanol*—Ethanol (denatured containing no measurable sulfate) is weighed into a container (equipped with a closure to prevent evaporation) in accordance with Table 1 to achieve the desired standard. Aqueous sulfate stock solution from 8.3 is added to the solution in accordance with Table 1, and the final weight of the solution recorded. Standards should be remade weekly or if recovery of less than 90% is noted. The concentration of the standard is calculated by dividing the number of milligrams sulfate from the sulfate stock solution and dividing by the final solution weight in accordance with Eq 3.

$$\text{EtOH Sulfate Standard (mg/kg)} = \frac{V \times C}{W} \tag{3}$$

V = volume of aqueous sulfate stock (8.3), mL,
C = concentration of aqueous sulfate stock (8.3), mg/L, and
W = final weight of ethanol and aqueous sulfate stock aliquot, g.

TABLE 1 Preparation of Sulfate Standards in Ethanol

Ethanolic Sulfate Standard, mg sulfate/kg ethanol	Ethanol, g	Aqueous Sulfate Stock Solution, mL
50	975	25
20	990	10
10	995	5
5	997.5	2.5
1	999.5	0.5

8.5 *Aqueous Sulfate Blank Solution, 0.01 M*—This is the same solution as in 8.2. This solution contains sulfate and will be added to all samples to allow a measurable sulfate blank to be measured.

8.6 *Dilute Perchloric Acid, 0.1 M*—Dissolve 8.8 mL perchloric acid (7.3) in 250-mL water in a 1-L volumetric flask. Mix well and dilute to the mark with Type III water.

8.7 *Lithium Chloride in Ethanol, 1 M*—Add lithium chloride (8.49 g) to absolute ethanol (200 mL) while stirring until it is dissolved.

9. Titration Equipment Preparation

9.1 *Titrator*—Prepare the titrator by filling the titrator reservoir with lead titrant (8.1). Follow the manufacturer's procedure for filling the buret. Perform titrations in monotonic titration mode, using either 25-µL or 50-µL titrant addition increments. Use a 10 mV/min drift condition or 20-s wait time between additions (whichever is achieved first).

9.2 *Electrode Preparation*—Proper care of the lead–selective electrode is essential for obtaining high–quality titration curves. Preparation of the lead electrode should be performed as specified by the manufacturer. A lead electrode utilizing a solid crystal sensor requires polishing when performance deteriorates. The voltage range for a 10 ppm sulfate in ethanol titration should span at least 50 mV and produce an acceptably shaped titration curve (see Fig. 1). If this level of electrode performance is not met, this indicates a need for lead electrode polishing. The lead electrode normally comes supplied with a polishing grit and a cloth rectangle. The polishing grit medium is placed on the cloth, wet with ethanol or water, moved over the surface of the cloth for a minute, rinsed with water to remove the polishing medium, and wiped dry with a tissue. The electrode is then soaked in lead titrant (8.1) for 2 min to re-equilibrate the electrode surface. The double junction reference electrode is filled with 1 M lithium chloride in absolute ethanol (8.7) in the outer chamber.

10. Standardization

10.1 Measure the exact concentration of the lead nitrate titrant by titration of the sulfate standard (8.2).

10.1.1 Transfer 1.00 mL of the 0.01 M aqueous sulfate standard solution (8.2) into a 150-mL beaker. Record this volume as *V*.

10.1.2 Add approximately 100 mL of denatured ethanol (7.4) and 1 mL of 0.1 M perchloric acid (8.6).

10.1.3 Prepare the autotitrator for operation, immerse the electrodes in the titration solution, initiate stirring, and titrate to the potentiometric endpoint with lead titrant. Titration should require approximately 4.0-mL of lead solution to reach the endpoint. Record this volume as *T*.

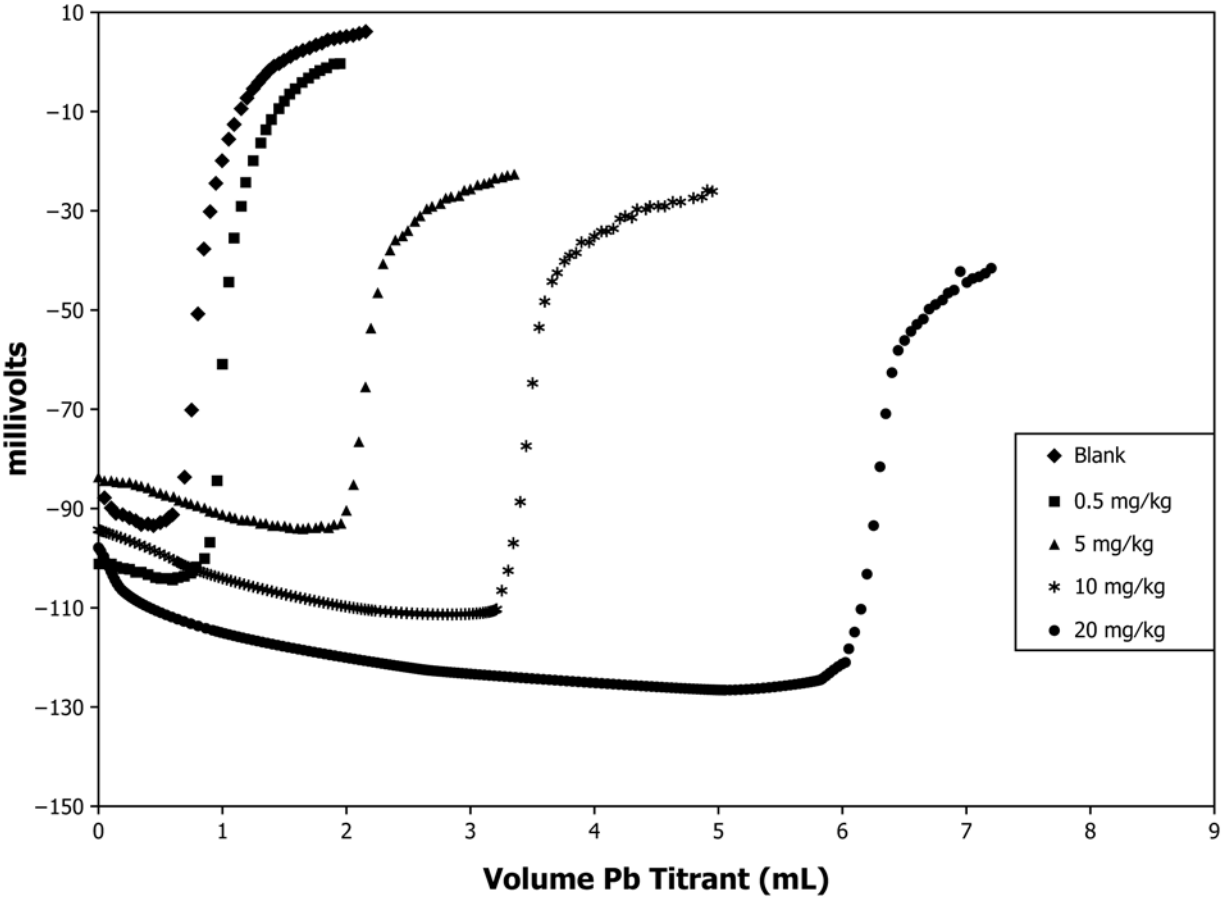

FIG. 1 Potentiometric Titration Curves for Sulfate Standards in Ethanol

10.2 Titrate a blank denatured ethanol sample in the same manner without addition of sulfate standard. Record this volume as T_b.

10.3 Calculate the concentration of the lead nitrate titrant as shown in Eq 4. The standardization should be repeated until precision comparable to that shown in Section 15 and Table 2 has been achieved.

$$M_{Pb} = \frac{V \times S}{T - T_b} \tag{4}$$

where:

M_{Pb} = molarity of lead in the titrant, mol/L,
V = volume of sulfate standard solution added, mL (10.1.1),
S = molarity of the sulfate solution from 8.2, mol/L,
T = volume of lead titrant used to titrate the sulfate solution, mL, and
T_b = volume of lead titrant used for the blank, mL (10.2).

11. Procedure

11.1 *Sample Analysis*—Obtain an ethanol sample in accordance with Practice D4057 or Practice D4177. The sample should be well mixed to ensure homogeneity. A representative portion shall be taken for analysis. Samples should be collected in containers with closures that seal well to prevent evaporation of ethanol. Samples containers should not contain any residual sulfate. If containers have been cleaned and rinsed with water, they must be rinsed with Type III water and dried prior to use.

11.2 *Blank Measurement:*

11.2.1 Determine the blank value by analysis of a denatured ethanol sample used for making standards (100 g) using the procedure described in 11.3. An aliquot of aqueous sulfate blank solution (8.5) is added to all samples as part of the blank. This is necessary to provide a stable blank value.

11.2.2 The average of three blank measurements is recorded as V_b for use in the calculation of sulfate content of samples.

11.3 *Sample Measurement:*

11.3.1 Accurately weigh an ethanol sample or blank (approximately 100 g) into a 150-mL beaker, and record the weight as G.

11.3.2 Carefully pipet 0.200 mL of aqueous sulfate blank solution (8.5) into the beaker containing the ethanol sample.

11.3.3 Add 1 mL of 0.1 M perchloric acid (8.6). The sample should be slightly acidic to pH paper before titrating, pH should be in the range of 3 to 5. The pH can be checked by dipping a glass stirring rod into the sample and testing a droplet on the rod with a moistened pH test strip. If 1 mL of 0.1 M perchloric acid is insufficient to achieve a pH in the range of 3 to 5, add an additional millilitre of acid and recheck the pH.

11.3.4 To prepare the autotitrator for operation, immerse the electrodes in the titration solution, initiate stirring and titrate to the potentiometric endpoint with lead titrant. Record the volume of titrant used as V.

11.3.5 Duplicate determinations should agree to within the repeatability limits in Section 15 and Table 2. If not, additional titrations should be performed until agreement is achieved.

11.3.6 If satisfactory titration curves are not obtained, the lead electrode should be polished (9.2). Typical titration curves for sulfate standards in denatured ethanol are shown in Fig. 1, and examples from commercial denatured ethanol samples are shown in Fig. 2.

TABLE 2 Test Method Precision

Analyte	mg/kg	Repeatability (*r*)	Reproducibility (*R*)
Existent Inorganic Sulfate	1.0	0.18	0.60
	4.0	0.25	0.85
	20.0	0.38	1.30

12. Calculation or Interpretation of Results

12.1 Calculate the inorganic sulfate content of the ethanol sample as follows in accordance with Eq 5:

$$\text{Sulfate (mg/kg)} = \frac{(V - V_b)(M_{Pb})(F)}{G} \tag{5}$$

where:

Sulfate = sulfate concentration, mg/kg,
V = volume of lead titrant for sample, mL (11.3.4),
V_b = average volume of lead titrant for blank, mL (11.2.2),
M_{Pb} = molarity of lead titrant, mol lead/L (as calculated by Eq 4),
F = factor, 96058 mg Sulfate/mol Sulfate, and
G = weight of ethanol sample taken for analysis, g (11.3.1).

12.2 The units of mg/kg can be converted to mg/L by multiplying the result by the density of denatured ethanol using Eq 6. Denatured ethanol density may be measured using Test Method D4052. However, for the purposes of this test method, all calculations should use mg/kg, weight/weight units.

$$\text{Sulfate (mg/L)} = \text{Sulfate (mg/kg)} \times D \tag{6}$$

where:

D = density of denatured ethanol, g/mL.

13. Report

13.1 Report the sulfate content results to the nearest 0.01 mg/kg over the 1.0–20 mg/kg range.

14. Quality Control (QC)

14.1 Confirm the performance of the instrument or the test procedure by analyzing one or more quality check sample(s) after each calibration and on at least each day of use thereafter. For example, a good check sample could be a single representative ethanol sample (see X1.5) that is analyzed repetitively. These results are plotted in control charts to check the system for statistical stability, as in X1.3.

14.1.1 When QC/Quality Assurance (QA) protocols are already established in the testing facility, they can be used when they confirm the reliability of the test result.

14.1.2 When there is no QC/QA protocol established in the testing facility, Appendix X1 can be used to define a suitable QC/QA system.

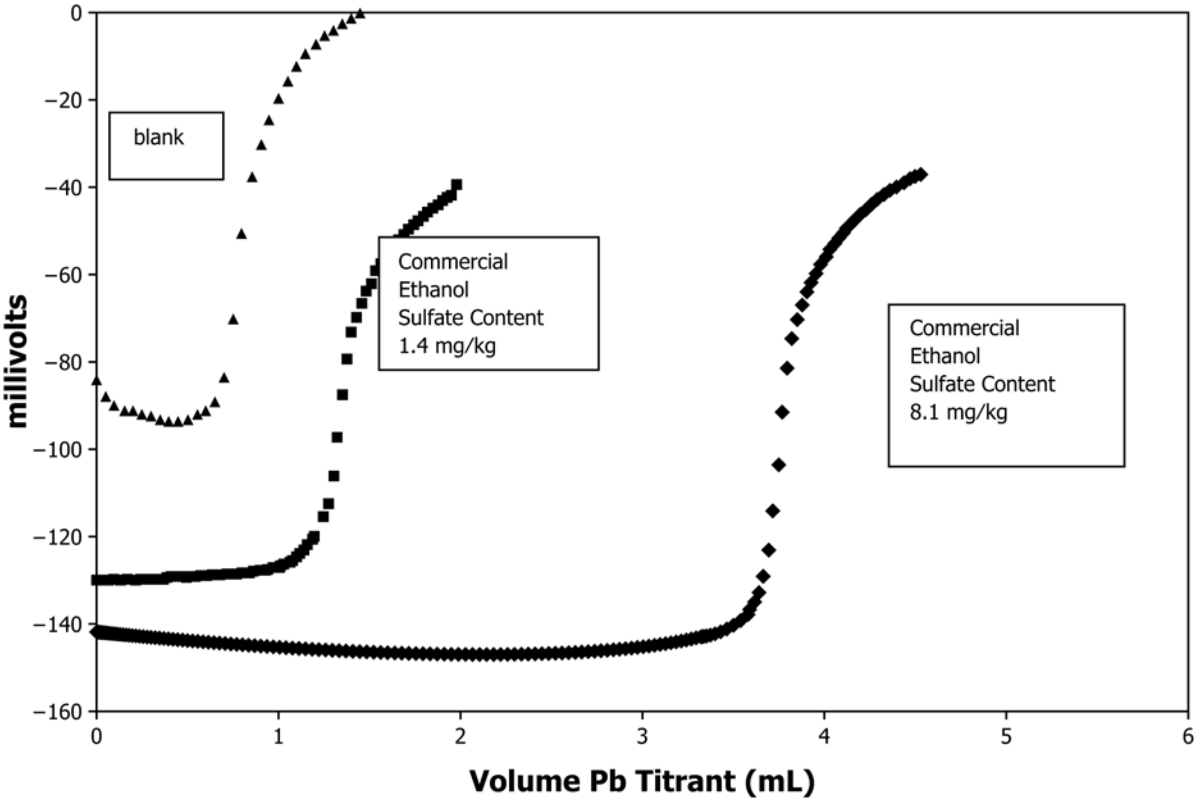

FIG. 2 Potentiometric Titration Curves for Existent Inorganic Sulfate in Commercial Denatured Ethanol

15. Precision and Bias[3]

15.1 *Precision*—The precision of this test method as determined by the statistical evaluation of the interlaboratory test results is as follows:

15.1.1 *Repeatability*—The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method exceed the following values only in one case in twenty.

15.1.1.1 *Existent Inorganic Sulfate*—The pooled limit of quantitation (PLOQ) is 1.0 mg/kg. Repeatability r between 1.0 and 20 mg/kg existent inorganic sulfate measured is calculated as follows:

$$r = 0.1711\left((X+0.1301)^{0.2678}\right) \quad (7)$$

where:

X = analyte concentration, mg/kg.

15.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method exceed the following values only in one case in twenty.

15.1.2.1 *Existent Inorganic Sulfate*—Reproducibility R between 1.0 and 20 mg/kg existent inorganic sulfate measured is calculated as follows:

$$R = 0.5807\left((X+0.1301)^{0.2678}\right) \quad (8)$$

where:

X = analyte concentration, mg/kg.

15.2 *Bias*—Since there was no generally accepted reference material available at the time of the interlaboratory testing, no statement of bias can be made at this time.

15.3 Table 2 shows precision values calculated from Eq 7 and Eq 8.

16. Keywords

16.1 ethanol; existent inorganic sulfate; lead; potentiometric; sulfate; titration

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[3] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1615.

APPENDIX

X1. QUALITY CONTROL (QC)

X1.1 Confirm the performance of the instrument or the test procedure by analyzing a quality control sample.

X1.2 Prior to monitoring the measurement process, the user of the test method needs to determine the average value and control limits of the QC sample (see Practice D6299 and MNL7[4]).

X1.3 Record the QC results and analyze by control charts or other statistically equivalent techniques to ascertain the statistical control status of the total testing process (see Practice D6299 and MNL7[4]). Any out-of-control data should trigger investigation for root cause(s). The results of this investigation may, but not necessarily, result in instrument recalibration.

X1.4 In the absence of explicit requirements given in the test method, the frequency of QC testing is dependent on the criticality of the quality being measured, the demonstrated stability of the testing process, and customer requirements. Generally, a QC sample is analyzed each testing day with routine samples. The QC frequency should be increased if a large number of samples are routinely analyzed. However, when it is demonstrated that the testing is under statistical control, the QC testing frequency may be reduced. The QC sample precision should be checked against the ASTM test method precision to ensure data quality.

X1.5 It is recommended that, if possible, the type of QC sample that is regularly tested be representative of the material routinely analyzed. An ample supply of QC sample material should be available for the intended period of use, and must be homogeneous and stable under the anticipated storage conditions. See Practice D6299 and MNL7[4] for further guidance on QC and control charting techniques.

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[4] MNL 7, *Manual on Presentation of Data Control Chart Analysis*, 6th ed., ASTM International, W. Conshohocken, PA.

SUMMARY OF CHANGES

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D7318 – 11) that may impact the use of this standard.

(1) Revised the definition in 3.1.1 and added a new definition in 3.1.2.