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A Single-Operator Study of the Florida Method of Test for Determining Low Levels of Chloride in Concrete and Raw Materials (FM 5-516)

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16. Abstract

The goals of this research were to establish for each matrix—concrete, coarse aggregate, fine aggregate, and cement—the relative bias, relative precision, and method limit of detection (LOD) for chloride ions extracted from concrete in accordance with FM 5-516; to determine which, if any, method factor when perturbed yields a statistically significant difference in chloride concentration; to recommend method revisions; and to develop a protocol for an inter-laboratory study to validate the revised method. The method limit of detection (LOD) for FM 5-516 was 0.10 lbs/yd^3, based on single-operator testing of two samples of concrete and one sample of cement with chloride content near the LOD. Rock and sand samples had chloride concentrations below the LOD. Accuracy and precision estimates for a 183-ppm (~1.0 lbs/yd^3) NIST SRM 1880b Portland cement were -3.27 % and 2.43 %, respectively, in contrast to estimates of 25.6 % and 1.78 % for a laboratory control sample concrete. The suspected cause of the large systematic error was the inaccuracy of the titrant delivery system in combination with an acidic sample extract. Many of the acid extracts of concrete, rock, and sand were below pH 2—that is, at a pH outside the operating range for both silver/sulfide and chloride electrodes. Below pH 2 a shift in junction potential occurs that can lead to an over-estimate of chloride content if no adjustment is made for this shift. The consequences of such a shift were mitigated by lowering the method's scaling potential by ~30 mV and by using a method blank to correct the chloride end point. Method performance was sensitive to titrant concentration and delivery volume, along with factors such as acid volume and strength that contributed to a shift in junction potential. A proposed revision to FM 5-516 incorporates additional QA/QC measures and increases the sample mass of concrete such that the sample extract is greater than pH 2.

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SI* (MODERN METRIC) CONVERSION FACTORS

APPROXIMATE CONVERSIONS TO SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol
		LENGTH		
in	inches	25.4	millimeters	mm
ft	feet	0.305	meters	m
yd	yards	0.914	meters	m
mi	miles	1.61	kilometers	km
		AREA		
in^2	square inches	645.2	square millimeters	mm^2
ft^2	square feet	0.093	square meters	m^2
yd^2	square yard	0.836	square meters	m^2
ac	acres	0.405	hectares	ha
mi^2	square miles	2.59	square kilometers	km^2
		VOLUME		
fl oz	fluid ounces	29.57	milliliters	mL
gal	gallons	3.785	liters	L
ft^3	cubic feet	0.028	cubic meters	m^3
yd^3	cubic yards	0.765	cubic meters	m^3
		NOTE: volumes greater than 1000 L shall be shown in m^3		
		MASS		
oz	ounces	28.35	grams	g
lb	pounds	0.454	kilograms	kg
T	short tons (2000 lb)	0.907	megagrams (or "metric ton")	Mg (or "t")
		TEMPERATURE (exact degrees)		
°F	Fahrenheit	5 (F-32)/9 or (F-32)/1.8	Celsius	°C
		ILLUMINATION		
fc	foot-candles	10.76	lux	lx
fl	foot-Lamberts	3.426	candela/m^2	cd/m^2
		FORCE and PRESSURE or STRESS		
lbf	poundforce	4.45	newtons	N
lbf/in^2	poundforce per square inch	6.89	kilopascals	kPa

APPROXIMATE CONVERSIONS FROM SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol
		LENGTH		
mm	millimeters	0.039	inches	in
m	meters	3.28	feet	ft
m	meters	1.09	yards	yd
km	kilometers	0.621	miles	mi
		AREA		
mm^2	square millimeters	0.0016	square inches	in^2
m^2	square meters	10.764	square feet	ft^2
m^2	square meters	1.195	square yards	yd^2
ha	hectares	2.47	acres	ac
km^2	square kilometers	0.386	square miles	mi^2
		VOLUME		
mL	milliliters	0.034	fluid ounces	fl oz
L	liters	0.264	gallons	gal
m^3	cubic meters	35.314	cubic feet	ft^3
m^3	cubic meters	1.307	cubic yards	yd^3
		MASS		
g	grams	0.035	ounces	oz
kg	kilograms	2.202	pounds	lb
Mg (or "t")	megagrams (or "metric ton")	1.103	short tons (2000 lb)	T
		TEMPERATURE (exact degrees)		
°C	Celsius	1.8C+32	Fahrenheit	°F
		ILLUMINATION		
lx	lux	0.0929	foot-candles	fc
cd/m^2	candela/m^2	0.2919	foot-Lamberts	fl
		FORCE and PRESSURE or STRESS		
N	newtons	0.225	poundforce	lbf
kPa	kilopascals	0.145	poundforce per square inch	lbf/in^2

*SI is the symbol for the International System of Units. Appropriate rounding should be made to comply with Section 4 of ASTM E380.

Executive Summary

The goals of this research were to establish for each matrix—concrete, coarse aggregate, fine aggregate, and cement—the relative bias, relative precision, and method limit of detection (LOD) for chloride ions extracted from concrete in accordance with FM 5-516; to determine which, if any, method factor when perturbed yields a statistically significant difference in chloride concentration; to recommend method revisions; and to develop a protocol for an inter-laboratory study to validate the revised method.

The method limit of detection (LOD) for FM 5-516 was 0.10 lbs/yd^3, based on single-operator testing of two samples of concrete and one sample of cement with chloride content near the LOD. Rock and sand samples had chloride concentrations below the LOD.

Many of the acid extracts of concrete, rock, and sand were below pH 2—that is, at a pH outside the operating range for both silver/sulfide and chloride electrodes. Below pH 2 electrode potentials shifted downward. Without a chloride end point correction using a likewise acidic (method) blank to correct for this shift, chloride content was over-estimated; significantly over-estimated for sand and rock that had little or no alkalinity. The consequences of such a shift were mitigated by lowering the method's scaling potential by ~30 mV and by using a method blank to correct the chloride end point.

Accuracy and precision estimates for a 183-ppm (~1.0 lbs/yd^3) NIST SRM 1880b Portland cement extracted and analyzed according to FM 5-516 were -3.27 % and 2.43 %, respectively, in contrast to estimates of 25.6 % and 1.78 % for LCS concrete 4474. The suspected cause of the large systematic error seen for concrete 4474 is the inaccuracy of the titrant delivery system in combination with an acidic sample extract.

Below a chloride content of ~0.10 lbs/yd^3 in hardened concrete, cement, and coarse and fine aggregates, the accuracy and precision of FM 5-516 rapidly degraded. Above this chloride content, repeatability standard deviation s_r increased but relative standard deviation RSD% (or coefficient of variation , CV) decreased with increasing chloride content over the range of chloride content studied.

Sensitivity of FM 5-516 to perturbation in method factors was explored for concretes 4473 and 062, for average chloride contents of 0.414 lbs/yd^3 and 0.119 lbs/yd^3, respectively. Hypothesis testing of replicated results of small changes in individual factors revealed that errors in sample weight, titrant concentration, titrant delivery volume, stirring rate, or amount of added acid, as examples, significantly affected either the measured chloride content or its standard deviation, or both. Simulations of inter-laboratory study data for each of these concretes were reasonably consistent with results from an earlier study by Kessler et al. (1982), except that the maximum allowable range calculated for concrete 4473 was 0.14 lbs/yd^3, which is greater than the value of 0.080 lbs/yd^3 estimated by Kessler et al. (1982) for a concrete of similar chloride content.

Proposed revisions to FM 5-516 target reductions in leveraged sources of variability, including performance specifications for equipment such as bottle-top dispensers used to deliver titrant or acid.

Suggested improvements to the method generally fell into one of three categories: one, reducing ambiguity in the method; two, adding QA/QC steps to the method; and three, addressing the issue with low pH measurements. Key recommendations for a future version of FM 5-516 include:

- Daily or more frequent testing of one or more laboratory control samples (LCS) prepared at chloride content of ~0.10 lbs/yd^3 to provide input data for method software to automatically calculate and trend the method LOD;
- Routine analyses and trending of chloride content in chloride check standards (CCS) and laboratory control standards (LCS) to assure that titrant delivery (concentration and volume) are under control;
- An increased mass of pulverized hardened concrete that is extracted for chloride such that the final extract has pH > 2 and a decreased mass of powdered cement such that the final extract has pH < 8;
- Addition of a cement LCS to pulverized non-alkaline samples such as rock or sand such that the resulting extract has pH > 2;
- Specified tolerance of the titrant delivery system and required daily checks of titrant delivery volume accuracy using at least 10 cumulative 0.5-mL volumes;
- Shewhart charts or similar tools integrated into method software to trend QA/QC measurements such as titration end points or chloride content in blank, chloride check, and laboratory control samples and to provide an indication when the method is out of control. A minimum sequence of 20 samples is recommended along with a chart "window" that moves such that only the most recent "in control" samples are included in the chart.

Development of precision and bias statements for the revised FM 5-516 has two stages: first, a ruggedness study to be accomplished in accordance with ASTM C1067 (2007), and second, an inter-laboratory study to be done in accordance with ASTM 802 (2009). The product of the first stage is a method that is in its final form for the inter-laboratory study. Proposed for the second stage is a 10-laboratory study where samples at five target levels of chloride: 0.10, 0.25, 0.40, 0.70, and 2.5 lbs/yd^3 are presented as cylinders of hardened concrete to participating laboratories in four round-robins, where each round-robin is separated by two weeks. In such a study, performance of FM 5-516 yields one test result. Laboratories recruited for this effort must qualify on the revised FM 5-516 prior to the start of the study.

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Acknowledgements

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1 Introduction

1.1 Background

Chlorides enter concrete by two general pathways: in the preparation of concrete as part of the cement, fine aggregate, coarse aggregate, admixtures, or water; and upon exposure to the environment (Li and Sagüés, 2001). Once in concrete, chloride can initiate and accelerate the corrosion of reinforcing steel (Li and Sagüés, 2001). Chloride content limits for concrete construction allowed by the Florida Department of Transportation (FDOT) are summarized in Table 1-1.

Table 1-1 Chloride Content Limits for Reinforced Concrete

Application/Exposure Environment		Maximum Allowable Chloride Content, lbs/yd^3
Non-reinforced concrete		No Test Needed
Reinforced Concrete	Slightly Aggressive Environment	0.70
	Moderately or Extremely Aggressive Environment	0.40
Prestressed Concrete		0.40

Source: FDOT (2010) Section 346-4.2, Table 4

FDOT (2010) requires that concrete producers obtain and test a sample from each concrete mix design for chloride content on the first day of production and every 30 calendar days afterwards. Chloride testing must be done in accordance with Florida Method 5-516 (FM 5-516) by a qualified laboratory within 10 days and made available to the concrete producer within 14 calendar days of sampling (FDOT, 2009; FDOT 2010).

FM 5-516 is similar to two other methods, AASHTO T260 (2001) and ASTM D512 (2004); however, ASTM D512 (2004) is for chloride in natural waters, drinking water, and wastewater and thus does not include the steps for extracting chloride from concrete. Moreover, the ion-specific electrode method of ASTM D512 (2004) compares the electrode measurement in the water sample with a calibration curve derived from electrode measurements made from sodium chloride standards, which is substantially different than the Gran plot obtained by FM 5-516 or AASHTO T260 (2001). The most obvious difference between FM 5-516 and AASHTO T260 (2001) is the technique for pulverizing the concrete: the former method is better adapted to testing concrete poured and hardened in standard cylinder molds and the latter to testing concrete from an existing structure. Refer to Table A-1, Appendix A, at the end of this document for a summary of similar features between these three methods.

Determination of low chloride levels in concrete is a challenge because of lack of homogeneity between and within concrete mixes and interactions of mix ingredients with reagents that are commonly used in test methods. As a consequence, calibration of a method with a standard solution does not always assure either accurate or precise chloride determination in hardened concrete or in its constituents of sand, rock, and cement (Miller, 2009). Significant systematic errors can go undetected in a laboratory even when each step of the method is well-controlled and an internal reference material is periodically tested for quality control (Youden, 1975).

To diagnose systematic and random errors in an analytical chemistry method, periodic testing of a standard reference material (SRM) prepared by an outside laboratory and with well-defined properties of interest is recommended; participation in inter-laboratory comparisons is an extension of this approach (Youden, 1975; Miller, 2009).

1.2 Goals

The goals of this research were to establish for each matrix—concrete, coarse aggregate, fine aggregate, and cement—the relative bias, relative precision, and method limit of detection for chloride ions extracted from concrete in accordance with FM 5-516; to determine which, if any, method factor when perturbed yields a statistically significant difference in chloride concentration; to recommend method revisions; and to develop a protocol for an inter-laboratory study to validate the revised method.

1.3 Scope

This research had two phases. The first phase consisted of:

- A visit to two FDOT-approved laboratories to observe FM 5-516: one of these laboratories was the FDOT State Materials Office (SMO) Corrosion Laboratory in Gainesville;
- A pilot study to explore method factors including choice of electrode that are potentially significant contributors to the bias or precision of the measurements;
- A single-operator determination of the method limit of detection (LOD) and limit of quantification (LOQ) for each electrode;
- An assessment of accuracy based on analysis of National Institute of Standards and Technology (NIST) standard reference material (SRM) 1880b, Portland cement, with a certified chloride mass fraction of 0.01830 ± 0.00057%;
- A single-operator determination of method relative bias and relative precision;
- A test of the method sensitivity to factor perturbation for seven factors, tested on concrete 4473; and
- An interim report, including results from the first phase of research.

The second phase consisted of:

- A second visit to the FDOT SMO Concrete Corrosion Laboratory in Gainesville and a visit to a third FDOT-approved laboratory.
- A test of the method sensitivity to factor perturbation for seven factors, tested on concrete 062; and
- A final report, including results of research from both phases and proposed revisions to the method and a protocol for conducting an inter-laboratory study of revised method.

This research was conducted by Dr. Noreen Poor, Research Associate, in the laboratories of USF College of Public Health. FDOT's Materials Office provided powdered samples of concrete, coarse aggregate, fine aggregate, and cement consistent with the requirements of FM 5-516.

2 Overview of Method

2.1 Summary

For chloride acceptance testing, a representative amount of hardened concrete, cement, rock, or sand is collected from a supplier. FM 5-516 specifies the volume required for hardened concrete samples and the weights required for coarse and fine aggregate samples. In the laboratory, concrete is crushed into smaller chunks. All materials are dried in an oven and then pulverized to a powder such that the resulting particles can pass through a 0.300-mm opening. Powdered samples are stored covered in a clean, dry container.

Per FM 5-516, chloride is extracted from 3.000 g of a powdered sample by digestion for 3 min in 35.0 mL of boiling 1.20 N nitric acid. The resulting solution and residue are washed with hot de-ionized water into a filter. The chloride-containing solution drains by gravity through the filter into a 100-mL volumetric flask and is allowed to cool to room temperature, after which de-ionized water is added to bring the sample extract to volume.

Chloride content is determined by Gran titration. The sample extract is titrated with 0.500 mL increments of 0.0100 N silver nitrate whereby silver precipitates with chloride present in the extract. Voltage sensed with a silver/sulfide electrode is monitored with each added 0.500 mL aliquot of silver nitrate until the reaction end point has been passed, after which the next five voltages and cumulative volumes are recorded. A 100-mL solution of de-ionized water amended with 1.00 mL of concentrated potassium nitrate for ionic strength adjustment (ISA) serves as a blank to correct for background chloride concentration. The electrode voltage measured after adding 1.00 mL of 0.0100 N silver nitrate to the blank is defined as the "scaling" potential. During titration of a sample extract, a voltage reading that exceeds the scaling potential signals that the reaction end point has been passed.

Each sample is run in triplicate along with one blank. Paired voltage and cumulative volume measurements are manually entered into a SQL database that also calculates the titration end points and generates a report that includes the titration end points, replicate chloride concentrations, average chloride concentration, and chloride concentration range. High blank values generate a warning message.

For titration end point calculations, a linear model (Equation 1-1) is applied to a plot of Gran's function F versus cumulative titrant volume V (Gran, 1952). In Equation 1-1, V_o is the initial sample volume, E is the observed electrode voltage, k_1 is a constant potential, S is the electrode slope, k_2 is constant with units of moles/moles, and V_e is the volume of silver that was needed to reach the reaction end point. For the reaction of silver nitrate with chloride, the Nernstian electrode slope S is 0.0592 volts at 25 °C or 0.0580 volts at 20 °C. Chloride 2008 software incorporates a slope S of 0.0582 volts. The slope, y-intercept, and x-intercept for a linear model fit to Equation 1-1 are k_2, k_2V_e, and V_e, respectively.

$$F = (V_0 + V) \cdot 10^{(E-k_1)/S} = k_2(V - V_e) = k_2V - k_2V_e \qquad (2\text{-}1)$$

The end point volume V_e is then converted to a chloride concentration C_{cl} (ppm) according to Equation 2-2, where $V_{e(S)}$ and $V_{e(B)}$ are the titration end point volumes (mL) for sample and blank, respectively, C_{Ag} is concentration of silver nitrate (mol/L), AW_{Cl} is the atomic weight for chloride (g/mol), and W_0 is the sample mass (g) or water mass for standards. For units of lbs/yd^3, C_{cl} is converted back to a mass fraction and multiplied by the unit weight of the sample (Table 2-1).

$$C_{Cl} = \frac{(V_{e(S)} - V_{e(B)}) \cdot C_{Ag} \cdot AW_{Cl} \cdot 1000}{W_0} \qquad (2\text{-}2)$$

Table 2-1 Unit Weights

Material	Unit Weight, lbs/yd^3
Cement	5,307
Concretes 4470, 4471, 4472, 4473, 4474	3,915
Concrete 062	3,842
Rock	4,566
Sand	4,448

Equation 2-3 is an example for a 3-ppm chloride check standard (CCS) prepared in a 100-mL volumetric flask and Equation 2-4 is an example for 3 g of a 100 ppm chloride laboratory control standard (LCS) that is extracted in acid and diluted to 100 mL.

$$\frac{(0.8915\ mL - 0.0322\ mL)\cdot 10^{-3} mL/L \cdot 0.0100\ mol/L \cdot 35.45\ g/mol \cdot 10^{6} \mu g/g}{100.0 g} = 3.05 \frac{\mu g}{g} = 3.05\ ppm \qquad (2\text{-}3)$$

$$\frac{(0.8915\ mL - 0.0322\ mL)\cdot 10^{-3} mL/L \cdot 0.0100\ mol/L \cdot 35.45\ g/mol \cdot 10^{6} \mu g/g}{3.000 g} = 101 \frac{\mu g}{g} = 101\ ppm \qquad (2\text{-}4)$$

2.2 Development of the Method

Kessler et al. (1978) modified an existing potentiometric titration method (Berman, 1972, as cited in Kessler, et al., 1978) into a method intended for accurate and precise acceptance testing of hardened concrete for low levels of chloride. Their experimental studies led to decisions on method sample mass, concentration and amount of nitric acid for sample digestion, and scaling potential, as examples, and integration of a blank, Gran titration, and computer-aided data analysis into the method.

Methods similar to FM 5-516 are used by concrete laboratories around the world (Climent et al., 1999; Castellote and Andrade, 2001; Potgieter et al., 2004; Miller, 2009) with variations such as no filtration between extraction and analysis (Climent et al., 1999; Climent et al., 2004); replacement of nitric acid with acetic acid (Potgieter et al., 2004); and use of internal calibration with sodium chloride in lieu of Gran titration with silver nitrate (Clemeña and Apusen, 2002).

An inter-laboratory study was conducted to validate the new FM 5-516 (Kessler, 1982). In this study five laboratories analyzed pulverized concrete samples prepared at two chloride levels: 0.40 lb/yd^3 and 0.18 lb/yd^3; two samples were sent to each laboratory six months apart for a total of 10 triplicate analyses. In their data analysis, each replicate of a pulverized material sample was treated as a separate test result. Kessler et al. (1982) reported on overall means, within- and between-laboratory variances and their components, within- and between-laboratory standard deviations and coefficients of variations, and maximum individual standard deviation. They recommended keeping a chloride content limit of 0.40 lbs/yd^3 (Table 1-1) and decreasing the acceptable range of results from 0.15 lbs/yd^3 to 0.08 lb/yd^3.

3 Quality Assurance/ Quality Control (QA/QC)

3.1 Good Laboratory Practice

Obtaining measurement data of known quality is a goal as important today as it was three decades ago and can be achieved with appropriate QA/QC activities along with good laboratory practices such as those summarized below (ASTM D3856, 2006):

- A workspace that is clean, comfortable, and safe;
- Staff that have education and training appropriate for assigned tasks;
- Written procedures that provide clear direction for sample collection, handling, and storage, sample analysis, and calibration and maintenance of the measurement system;
- Supervision of laboratory staff to promote uniform and compliant performance of procedures;
- Recordkeeping to document equipment calibration, repair, and maintenance;
- A chemical hygiene plan;
- A system for tracking sample disposition and analyses;
- Recordkeeping to document QA/QC activities; and
- Communication and troubleshooting protocols for investigating out-of-control results.

3.2 QA/QC Activities

QA/QC activities that are appropriate for measurement of chlorides in solution by FM 5-516 are shown in Table 3-1 (ASTM D3856, 2006; FDEP, 2009). Refer to Appendix B for definitions of QA/QC terms.

Table 3-1 QA/QC Activities Appropriate for FM 5-516

Activity	Description	Purpose	Frequency
Calibration check (analytical balance)	Check the calibration of the analytical balance with Class S or better weight. Note: the watch glass used for weighing samples can serve as a transfer standard for checking balance calibration.	Assures that the analytical balance is in good working order.	Once per day at the start of sample analyses; once per year by an outside specialist; after maintenance or repair of balance
Calibration curve	Verify electrode calibration for the chloride working range (1 ppm to 10 ppm) from dilutions of a NIST-traceable stock standard solution of chloride. The supplier of this standard must be different from the supplier for the check standard.	Assures that the ISE electrode slope is within the manufacturer's recommended range, typically 54 to 60 mV/decade.	Once per day at the start of sample analyses.
Blank	Test a blank made from de-ionized (reagent) water.	Identifies contamination from reagent water.	At the start of sample analyses and one blank for every 24 analyses (8 samples)
Calibration (check) standard	Test chloride content in chloride check standard (CCS) prepared from a stock standard solution of chloride. Prepare stock standard solution from ACS-grade sodium chloride or NIST-traceable sodium chloride solution.	Assesses electrode accuracy and precision. Chloride recovery should be within 95% to 105%.	At the start of sample analyses and one CCS for every 24 analyses (8 samples).
Laboratory replicates	Analyze powdered sample in triplicate.	Provides an on-going check of method precision.	Every sample.
Matrix spike	Substitute 5 g of de-ionized water used to wet the concrete sample with 5 mL of a 100 mg/L (ppm) chloride standard solution.	Checks for matrix interferences. Chloride recovery should be within 85% to 115%, unless historical data indicate tighter limits can be routinely maintained.	On the suspicion of matrix interference.
Laboratory control sample (LCS)	Test chloride content in a hardened concrete LSC and a cement LCS prepared at chloride content near the method detection level.	Assesses method accuracy and precision and is used to calculate method LOD. Serves as a method blank to identify contamination from reagents, glassware, and materials handling.	At the start of sample analyses and one LCS for every 24 analyses (8 samples). Alternate concrete and cement LCS between batches.
Independent or standard reference material	Test chloride content in a NIST-traceable standard reference material (SRM), for example, a NIST SRM cement with certified chloride content.	Assesses method accuracy and precision. Identifies systematic errors. Chloride precision and recovery should not be statistically different that the NIST-certified value.	Once per quarter.

4 Method Limit of Detection (LOD) and Limit of Quantitation (LOQ)

4.1 Definition of LOD

The limit of detection (LOD) is defined by Ellison et al. (2009) as the "minimum concentration of the analyte that can reliably be detected with a specified level of confidence." The general features of an LOD experiment or a similar method detection level (MDL) experiment are (Clesceri et al., 1998; Ellison et al., 2009):

- 7 to 20 replicate samples containing either no analyte (blank samples) or a low-level of analyte are analyzed over a period of days;
- For analysis of a low-level of analyte, the analyte concentration should be in the range of 1 to 5 times the LOD; and
- For a method LOD (or method detection level MDL), replicate samples must be processed through the entire method.

LOD is calculated according to Equation 4-1 using the average blank concentration x_0 and standard deviation s, and the one-tailed Student's t value for the experimental degrees of freedom ν and at the specified error levels, for example, 95% for both Type I (probability of a false positive or α) and Type II (probability of a false negative or β) errors (Ellison et al., 2009). Refer to Table 4-1 for the value of k_1. For $x_0 = 0$, $k_1 = 1$, $\alpha = \beta = 0.05$, and number of samples N = 7, Equation 4-1 simplifies to Equation 4-2.

Table 4-1 Values of x_0 and k_1 for Use in Calculation of LOD

Validation study of LOD s based on:	Routine use of method	
	Will test results be baseline corrected?	
	Yes	No
Observations with independent baseline corrections	$x_0 = 0$; $k_1 = 1$	NA
Observations without independent baseline corrections	$x_0 = 0$; $k_1 = \sqrt{1 + \frac{1}{N_{bl}}}$, where N_{bl} = number of observations averaged to obtain the blank correction	$x_0 = x_{blank}$; $k_1 = 1$

Source: Ellison et al. (2009), Table 9-3, pg. 155.

$$LOD = x_0 + k_l s t_{(\nu,\alpha)} + k_l s t_{(\nu,\beta)} \qquad (4\text{-}1)$$

$$LOD = 3.88 \cdot s \qquad (4\text{-}2)$$

For comparison, MDL is calculated according to Equation 4-3, where the specified level of a Type I or α error is 99%, which simplifies for $\alpha = 0.01$ and N = 7 to Equation 4-4 (Clesceri, et al., 1998; FDEP, 2009):

$$MDL = st_{(\nu,\alpha)} \tag{4-3}$$

$$MDL = 3.14 \cdot s \tag{4-4}$$

4.2 Definition of LOQ

The limit of quantitation (LOQ), or similarly the practical quantitation limit (PQL), is defined as the "lowest concentration of analyte that can be determined with an acceptable level of uncertainty" (Ellison et al., 2009) and takes into account variations in LOD or MDL from laboratory to laboratory. Ellison et al. (2009) describes LOQ as 10 · s; Clesceri et al. (1998) as ~5 · MDL.

4.3 Calculation of Standard Deviation

FM 5-516 requires a baseline correction of chloride titration end points based on titration of a blank of de-ionized water amended with ISA (see Section 2.1 and Equation 2-2). The standard deviation associated with the baseline-corrected chloride concentration is given in Equation 4-5, where s_s is the sample standard deviation and s_{bl} is the blank standard deviation.

$$s = \sqrt{s_s^2 + s_{bl}^2} \tag{4-5}$$

If $s_s = s_{bl}$, then Equation 4-5 is simplified to $\sqrt{2}\,s$; in this case, $\sqrt{2}$ corresponds with k_1 in Table 4-1, where $N_{bl} = 1$; otherwise Equation 4-5 applies.

4.4 Calculation of LOD and LOQ

Refer to Table 4-2 for descriptive statistics for repeated measures of de-ionized water blanks and concrete and cement samples with chloride concentrations near the estimated method LOD. Except for concrete 062, potentiometric measurements were made with either a silver/sulfide electrode or a chloride electrode; for concrete 062, measurements were made with a silver/sulfide electrode. Placement of sample extracts on the hot plate and the sequence in which extracts were analyzed were randomized to reduce systematic errors. Distribution of chloride concentrations for the blanks and samples were not significantly different at the 95% confidence level from a normal distribution based on a Kolmogorov-Smirnov (K-S) test. Although sands and rocks were tested for chloride content, chloride concentrations were below the method LOD (refer to Section 5-2, Figures 5-1 through 5-3).

Table 4-2 Descriptive Statistics of Titration End Points for Blank and Sample Extract Solutions Used to Determine Method LOD (units in mL)

Statistic	Blank	Concrete 062	Concrete 4470	Cement Argos
Mean	0.033	0.296	0.327	0.262
Standard Error	0.004	0.008	0.015	0.011
Median	0.036	0.299	0.313	0.272
Mode	0.041	0.252	NA	NA
Standard Deviation	0.029	0.052	0.049	0.028
Sample Variance	0.001	0.003	0.002	0.001
Kurtosis	5.012	-0.648	1.289	-1.053
Skewness	-1.549	-0.062	0.258	-0.614
Range	0.168	0.238	0.191	0.074
Minimum	-0.083	0.176	0.236	0.222
Maximum	0.085	0.414	0.427	0.295
Sum	1.540	14.229	3.594	1.574
Count	47	48	11	6
Confidence Level (95.0%)	0.008	0.0152	0.033	0.029

An LOD calculated from the de-ionized water blank could be construed as an instrument LOD (or instrument detection level, IDL: Clesceri et al., 1998) and was calculated from Equation 4-1 and for comparison with concrete 062, was converted to units of lbs/yd^3 using a unit weight of 3,842 lbs/yd^3:

Instrument LOD = 0.033 + (2)(1)(0.029)(1.68) = 0.130 mL (0.059 lbs/yd^3).

Example calculations for concrete 062 are shown below:

- From Equation 4-5, $s = \sqrt{(0.052)^2 + (0.029)^2}$ = 0.059 mL
- From Equation 4-1, method LOD = (2)(1)(0.059)(1.68) = 0.200 mL (0.093 lbs/yd^3)

From concrete 4470 and cement Argos, computed method LODs were 0.098 lbs/yd^3 and 0.102 lbs/yd^3, respectively. The average method LOD was 0.098 lbs/yd^3, or ~0.10 lbs/yd^3. Method LOQs (Equation 4-3) for concrete 062, concrete 4470, and cement Argos were 0.275, 0.268, and 0.252 lbs/yd^3; the average method LOQ was ~0.27 lbs/yd^3.

Daily testing of one or more laboratory control samples (LCS) prepared at chloride content of ~0.10 lbs/yd^3 generates input data for method software to automatically calculate and trend the method LOD and to continuously test that the method is still in control.

4.5 Treatment of Blanks

A desirable characteristic of the distribution of blank chloride concentrations is that at the 95% confidence level, the blank concentration is below the LOD concentration. Likewise, a desirable characteristic of the LOD concentration is that at the 95% confidence level, the LOD concentration is below the target concentration. Replicate measurements of both blank and sample chloride concentrations are necessary to test these hypotheses, as illustrated by Figure 4-1. For this graph, blank and target chloride concentrations were 0.015 lbs/yd^3 and 0.300 lbs/yd^3, respectively, and standard deviations were calculated from Equation 6-8.

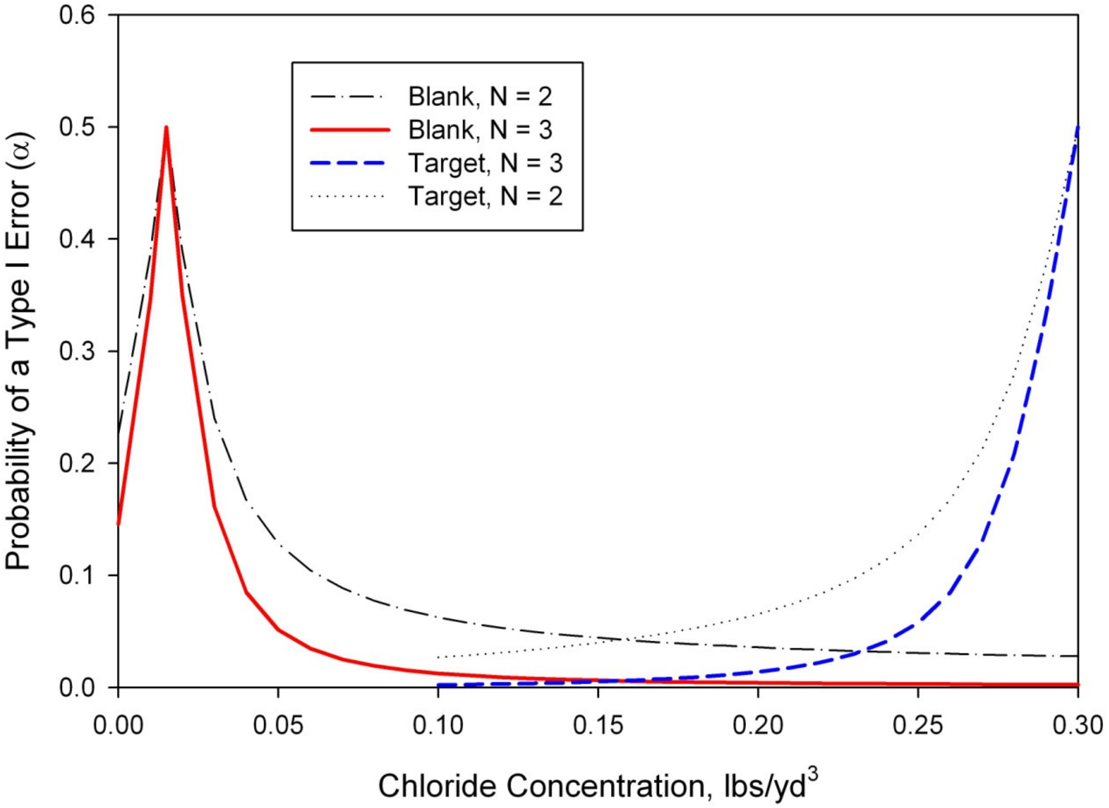

Figure 4-1. Probability of a type I error (α) versus blank and target chloride concentrations.

In this example, triplicate measures of blank and of sample (or standard) are sufficient to test that adequate separation exists between blank and LOD, sample and LOD, and blank and sample chloride concentrations. Duplicate measures of blank and of sample (or standard) are sufficient to test that adequate separation between sample and LOD, blank and sample, but not blank and LOD.

These results suggest a revised FM 5-516 should require triplicate measurements of blanks, standards, and samples to assure data quality; another approach is to use daily single or duplicate measures of blanks and standards but trend the data over time and use the trend statistics to assure data quality. With this latter approach, chloride titration end points for standards and samples are corrected to an average of the most recent 20 blank titration end points, for example, rather than to a single blank measurement. This concept is explored in more detail in Section 8.

4.6 Summary of Results

The limit of detection (LOD) for FM 5-516 was 0.10 lbs/yd^3, based on single-operator testing of two samples of concrete and one sample of cement with chloride content near the LOD.

Daily testing of one or more laboratory control samples (LCS) prepared at chloride content of ~0.10 lbs/yd^3 is recommended as input for method software to automatically calculate and trend the method LOD and to continuously test that the method is still in control. Likewise, daily testing of one or more de-ionized water blanks is recommended as input for method software to automatically trend the average blank titration end point for blank correction of standards and samples and to continuously test that the method is still in control.

5 Influence of pH on the Electrode Response

5.1 Overview of pH Influence

The recommended pH operating range for both silver/sulfide and chloride electrodes is pH 2 to 12; for Gran titration with silver nitrate the range narrows between pH 2 and 8 because at higher pH values the hydroxide ion precipitates with added silver to form Ag_2O (Thermo, 2007). Below pH 2 and above pH 12, mobility of the hydrogen and hydroxide ions, respectively, creates an interfering junction potential; calibration at the sample pH can mitigate this effect (Thermo, 2003). When prepared according to FM 5-516, sample extracts spanned pH values from less than 1 to greater than 9 (Table 5-1), with most sample extracts outside the recommended electrode operating range.

Table 5-1 pH Values for Concrete and Aggregate Acid Extracts

Matrix	Cements					Concretes						Rocks					Sand
Sample ID	Argos	40	41	42	43	62	4470	4471	4472	4473	4474	08-012	87-089	87-090	GA-383	GA-553	11-057
pH	9.68	9.41	9.19	9.27	9.51	1.34	1.40	1.30	1.21	1.21	1.35	5.89	3.84	6.09	1.05	1.08	0.54

Subsamples of concrete 4470 ranging in mass from 0.5 g to 6.0 g were analyzed in accordance with FM 5-516. Extracts that were titrated ranged from pH 0.86 to pH 8.56 for a 0.5 g and a 5.5 g subsample, respectively. The influence of low pH on chloride determination is clearly seen in Figure 5-1: below pH 2, the observed chloride content increases with decreasing pH as a power law function. Between pH 8 and 9 the influence of pH was not as strongly evident as for pH between 0 and 2. An argument can be made that pH affected the amount of chloride extracted from the sample, for example, that more chloride was extracted at lower pH and this argument merits further consideration.

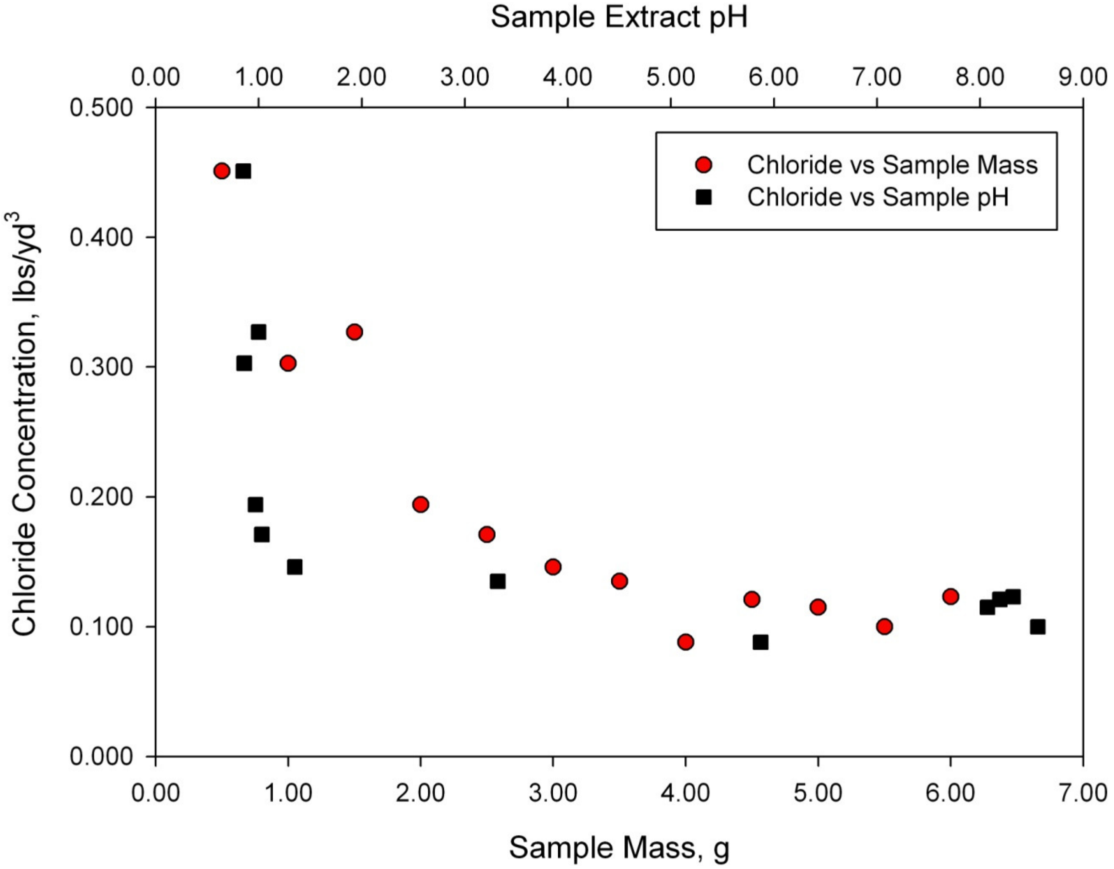

Figure 5.1. Chloride concentration versus mass of concrete sample and sample extract pH for concrete 4470.

5.2 <u>Exploration of pH Influence</u>

To investigate further the effect of pH on electrode response, chloride calibration curves were prepared for chloride concentrations from 1.00 mg/L to 10.0 mg/L (~$10^{-4.55}$ to $10^{-3.55}$ M). For each set of curves, calibration standards were made in either with no acid amendment, nitric acid amendment, or with nitric acid plus sodium hydroxide amendment. Standards prepared without acid or base additions were amended with potassium nitrate as an ionic strength adjustment per FM 5-516. Electrochemical potentials were measured with both silver/sulfide and chloride electrodes in each of the calibration standards (Figure 5-2).

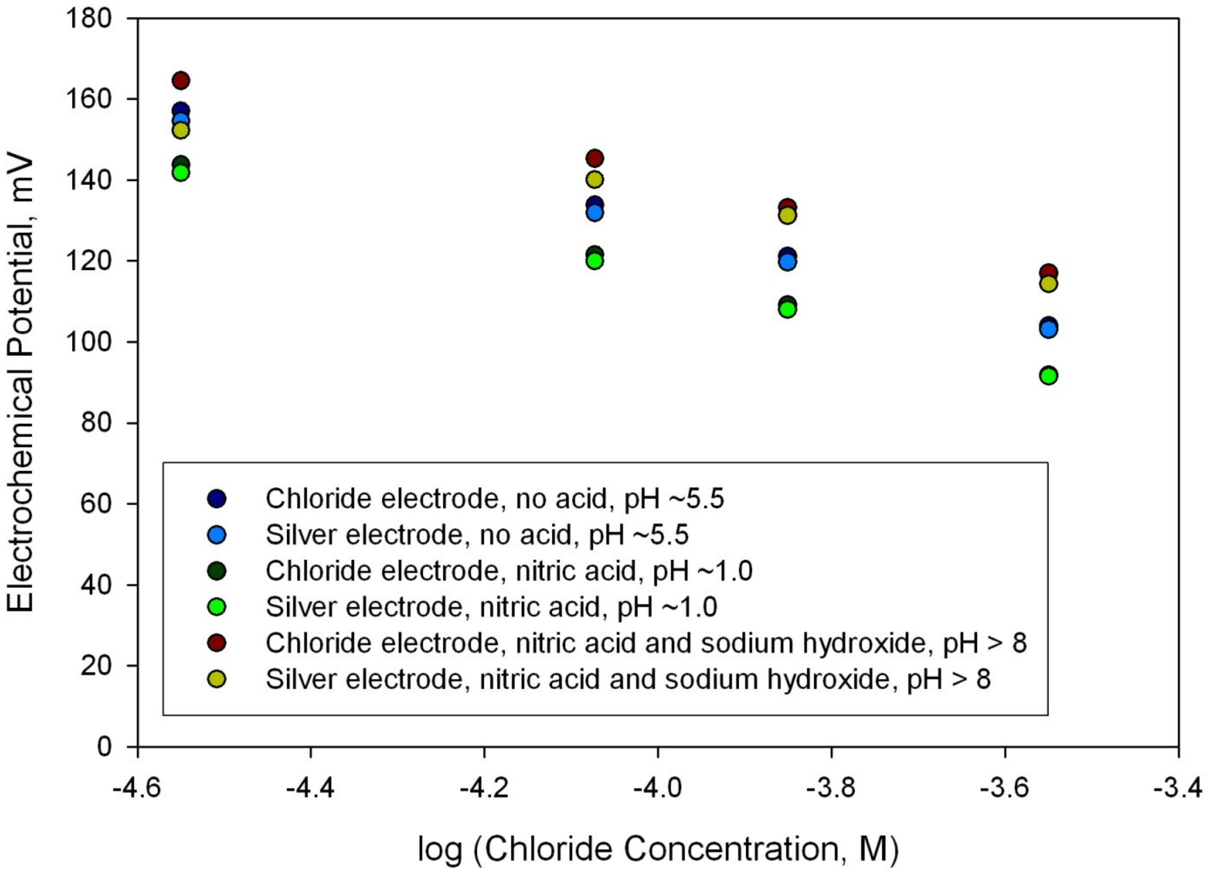

Figure 5-2. Response of electrode to pH of chloride calibration standards.

As seen in Figure 5-2, the slopes S of the calibration curves were similar at ~51 mV/M, but electrochemical potentials shifted downward for acidic standards and upward for basic standards. Electrode response in a complex matrix such as cement or concrete, however, is not likely to be this predictable.

Extracts of concrete, rock, and sand were below pH 2—that is, at a pH outside the operating range for the electrode. What are the consequences of executing a Gran titration according to FM 5-516 under these circumstances?

Figure 5-3 illustrates the effect of acid on electrode response for data from two blanks: an instrument blank and a method blank. Both blanks were prepared from de-ionized water and were analyzed on the same day with a silver/sulfide electrode. The instrument blank was amended with potassium nitrate for ionic strength adjustment; the method blank, however, was processed through acid extraction steps. The instrument blank was pH 5.7 and method blank was pH 0.92, the latter due to nitric acid addition. A scaling potential for FM 5-516 is determined by the electrode response to the addition of 1.00 mL of 0.01 N silver nitrate to an instrument blank and for either the combination silver/sulfide electrode or the combination chloride electrode is typically +227 mV.

Shown in Figure 5-3 are the data points that are used to calculate the chloride titration end point for the instrument blank and for the method blank treated either as a sample, that is, using a scaling potential of ~227 mV, or as a blank with a scaling potential of ~195 mV. The chloride titration end point for the instrument blank was 0.050 mL and for the method blank 0.350 mL and 0.073 mL for the higher and lower scaling potentials, respectively. Note that four additional 0.5 mL volumes were titrated to the method blank using a ~227 mV scaling potential when compared with the instrument blank. From Equation 2-1, the titration end point is the x-intercept of a line drawn through the data points. Small errors in either in silver nitrate concentration or delivery volume have large leverage because of the distance from the x-axis of data points used to determine the best-fit line. At a lower scaling potential data points taken are closer to the x-axis for a more accurate end point determination.

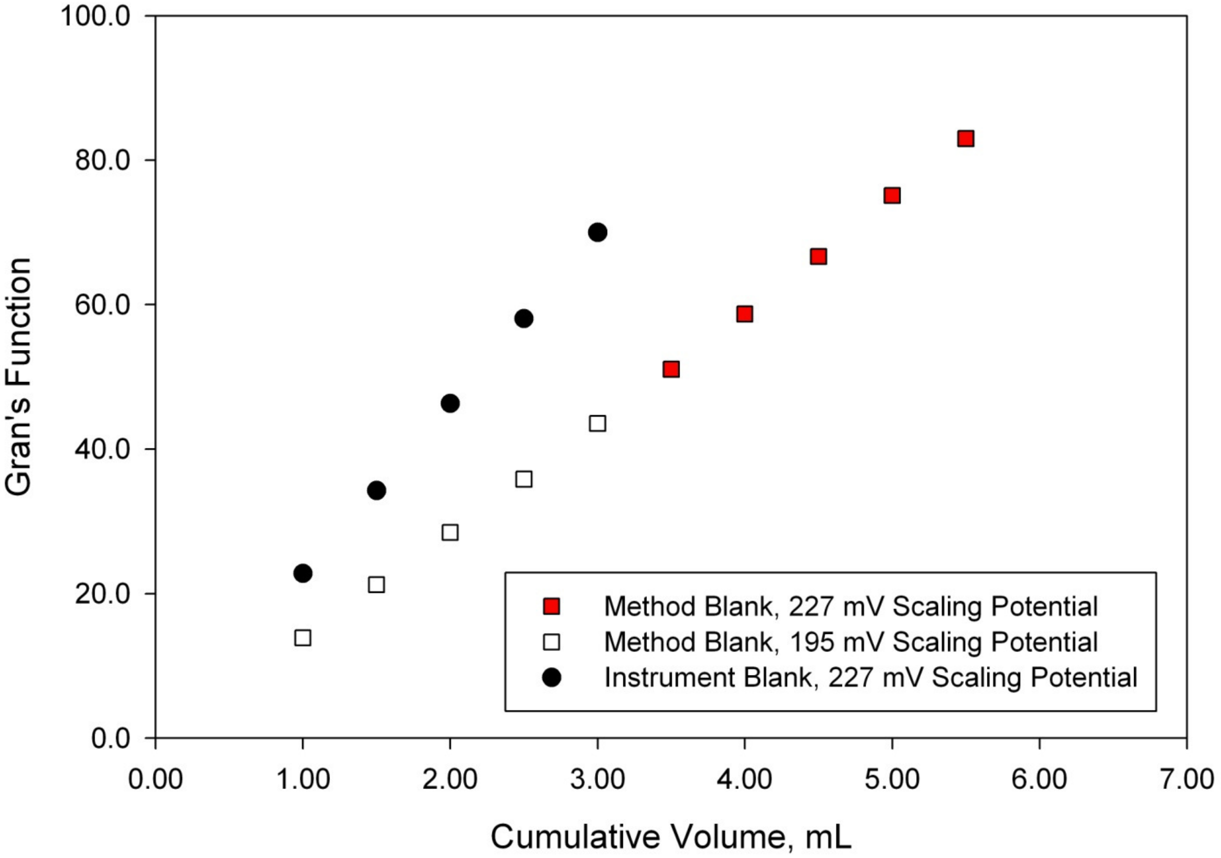

Figure 5-3. Comparison of Gran's function versus cumulative volume plots for a method blank and an instrument blank.

Shown in Figure 5-4 are the data points that are used to calculate the chloride titration end point for two check standards: an instrument check standard and a method check standard. Both calibration standards were prepared at 3 mg/L (ppm) chloride in de-ionized water. The instrument check standard was amended with potassium nitrate for ionic strength adjustment; the method check standard, however, was processed through acid extraction steps. Calibration standards were run on separate days but both were analyzed with a silver/sulfide electrode. No pH measurements were made, but presumably were near pH 5.50 for the instrument standard and pH 1.00 for the method standard, similar to the instrument and method blanks, respectively.

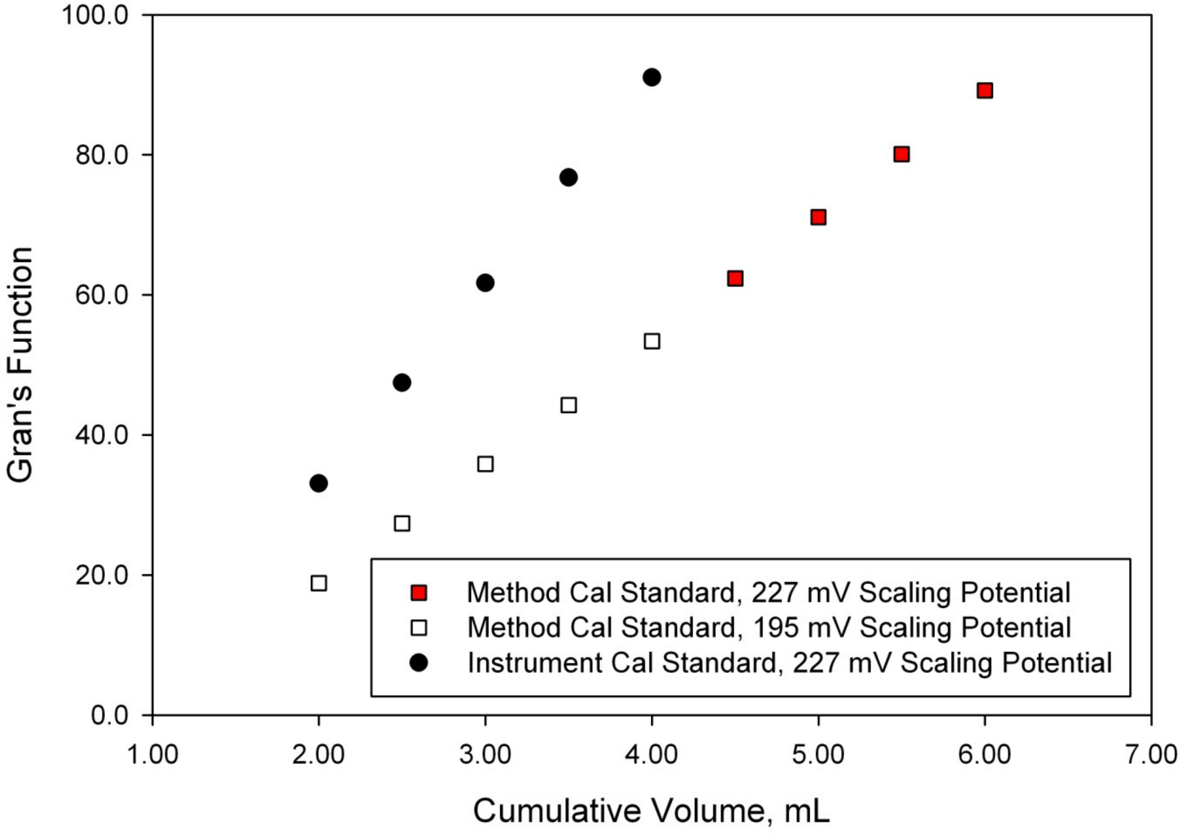

Figure 5-4. Comparison of Gran's function versus cumulative volume plots for a check standard and an instrument check standard.

Data points obtained for a scaling potential of ~227 mV yielded chloride titration end points of 0.871 mL and 1.100 mL for the instrument standard and the method standard, respectively. For the method standard, the corresponding end point for data points obtained with ~195 mV scaling potential was 0.914 mL. Note that the method standard was titrated with four additional 0.5 mL volumes for a ~227 mV scaling potential when compared with the instrument standard. As seen for the method blank, small errors in either in silver nitrate concentration or delivery volume have large leverage because of the distance from the x-axis of data points used to determine the best-fit line. At a lower scaling potential data points taken are closer to the x-axis for a more accurate end point determination.

Does the choice of scaling potential matter if a blank correction is made? If chloride concentrations are calculated for method calibration standards each corrected for a method blank obtained at the same scaling potential, the results for this example are 2.66 ppm chloride for a scaling potential of ~227 mV and 2.99 ppm chloride for a scaling potential of ~195 mV; the latter is closest to the expected value of 3.00 ppm chloride. If chloride concentrations are calculated for a method calibration standard and corrected for an instrument blank obtained at the same scaling potential of ~227 mV the resulting chloride concentration is 3.70 ppm.

In general, shifting the scaling potential downward will improve the method accuracy and precision, as data points thus acquired will be closer to the titration end point. The disadvantage of this approach is that closer to the titration end point, electrochemical potential measurements are less stable and more time is needed to get a stable reading. An alternative approach to bring data points closer to the x-intercept is to reduce the volume increment of silver nitrate delivered, for example, from 0.5 mL to 0.25 mL; an attendant disadvantage is the cost associated with obtaining accurate titrant delivery in 0.25 mL increments.

Use of an acidic blank, a lower scaling potential or a 0.25-mL titrant volume increment are not recommended for a future revision of FM 5-516 because these choices fail to correct the fundamental problem of a sample extract pH that is outside the normal operating range of the electrodes.

5.3 Summary of Results

In summary, many of the acid extracts of concrete, rock, and sand were below pH 2—that is, at a pH outside the operating range for both silver/sulfide and chloride electrodes. Below pH 2, chloride concentrations in samples, standards, and blanks were overestimated. Experimental results suggest that the influence of pH on chloride concentration in concrete extracts cannot be simply explained as higher chloride extraction efficiency but is consistent with an unwanted shift in junction potential. The consequences of such a shift were demonstrably mitigated by lowering the method’s scaling potential by ~30 mV and by using a method blank to correct the chloride end point.

6 Method Precision and Accuracy

6.1 Approaches to Calculating Accuracy and Precision

A measured value y is the sum of its unknown true value μ plus an unknown measurement error ε (Montgomery, 2005) (Equation 6-1), where ε consists of both a fixed component (bias) and a random component.

$$y = \mu + \varepsilon \qquad (6\text{-}1)$$

In many situations, unknown μ may be represented as known, for example, when μ is a certified, traceable, or consensus value or when μ was determined by a method with ε that is low in comparison to the method that produced y (Clesceri et al., 1998). If the random component of ε is negligible, the fixed component or bias of ε can be estimated from Equation 6-2.

$$\varepsilon = y - \mu = \varepsilon_{random} + \varepsilon_{bias} \tag{6-2}$$

A generalized expression of relative error RE is presented in Equations 6-3 for the case where μ is treated as known and y_i is the ith measure of y. The sign is retained to indicate the direction of bias.

$$RE\% = 100 \cdot \frac{1}{n} \sum_{i=1}^{n} \frac{(y_i - \mu)}{\mu} \tag{6-3}$$

For the case of unknown μ, however, Equation 6-4 is more appropriate.

$$RE\% = 100 \cdot \frac{(y_{max} - y_{min})}{\frac{1}{n} \sum_{i=1}^{n} y_i} = 100 \cdot \frac{(y_{max} - y_{min})}{\bar{y}} \tag{6-4}$$

The lower the RE% the more accurate is the method. For triplicate samples with chloride concentration range 0.08 lbs/yd^3 and average 0.40 lbs/yd^3, the relative error RE% is 20 % (Equation 6-4). This is the maximum error that is tolerated at the maximum allowable chloride content (Table 1-1).

Another and related measure of accuracy is the amount of analyte added to a sample (or matrix spike, see Appendix B for definition) that is recovered by the method. Recovery is calculated as using Equation 6-5, where C_{s+ms} is the chloride concentration in the sample with a matrix spike, C_s is the chloride concentration in the sample without a matrix spike, and C_{ms} is target concentration of the matrix spike.

$$Recovery\% = 100 \cdot \frac{C_{(s+ms)} - C_s}{C_{ms}} \tag{6-5}$$

The usual measure of data scatter is standard deviation σ and estimates of σ are represented at s, where s has both a random and a systematic component. Youden (1975) explains that the random component is determined from replicate measurements in the same laboratory under the same conditions, while the systematic component is introduced under differing conditions in the same laboratory, for example, another operator, or between laboratories. He notes that if other laboratories are not following the same procedures for reasons such as ambiguous instructions or undefined environmental factors, then random error will vary between laboratories as well. In general, however, the terms random and systematic are often used interchangeably with single-operator and multi-laboratory, respectively, in reference to components of variance.

Similar to Youden (1975), Clesceri et al. (1998) refers the random component of method standard deviation as the repeatability of a method s_r, which is estimated by pooling sample standard deviations s_{ri} of measurements of N different specimens as shown in Equation 6-6

(Clesceri et al., 1998). A standard deviation that characterizes both random and systematic errors is the reproducibility of a method s_R and is discussed further in Section 10. A method with lower s_r or s_R is a more precise method.

$$s_r = \sqrt{\frac{1}{N}\sum_{i=1}^{N} s_{ri}^2} \qquad (6\text{-}6)$$

Another and related measure of precision is the relative standard deviation RSD%, as defined in Equation 6-7, and applies generally to either σ or s; that it, to either population or sample statistics (Skoog et al., 1996); RSD% is synonymous with coefficient of variation (CV).

$$RSD\% = 100 \cdot \frac{s}{\bar{y}} = CV \qquad (6\text{-}7)$$

6.2 Trends in Measures of Accuracy and Precision

Relative errors RE% (Equation 6-4), standard deviations (Equations 4-5; 6-6), and relative standard deviations (Equation 6-7) were plotted against average chloride concentrations for concrete and aggregates in Figures 6-1, 6-2, and 6-3, respectively. Five sand and two rock samples had little or no apparent alkalinity so their titration end points were corrected to blanks that were run through the entire method such that they were as acidic as the samples. The estimated method LOD (Section 4-4) is shown on each of these plots.

Figures 6-1 and 6-3 clearly show the improvement in relative accuracy and relative precision with chloride concentration in concrete and cement at concentrations above the LOD. Figure 6-2 reveals that absolute precision declined with a power curve trend below the LOD but declined with a linear trend above the LOD. Kessler et al. (1982) found that standard deviations increased but coefficients of variations (CV) decreased with increasing chloride content in concrete samples that were tested as part of an inter-laboratory study.

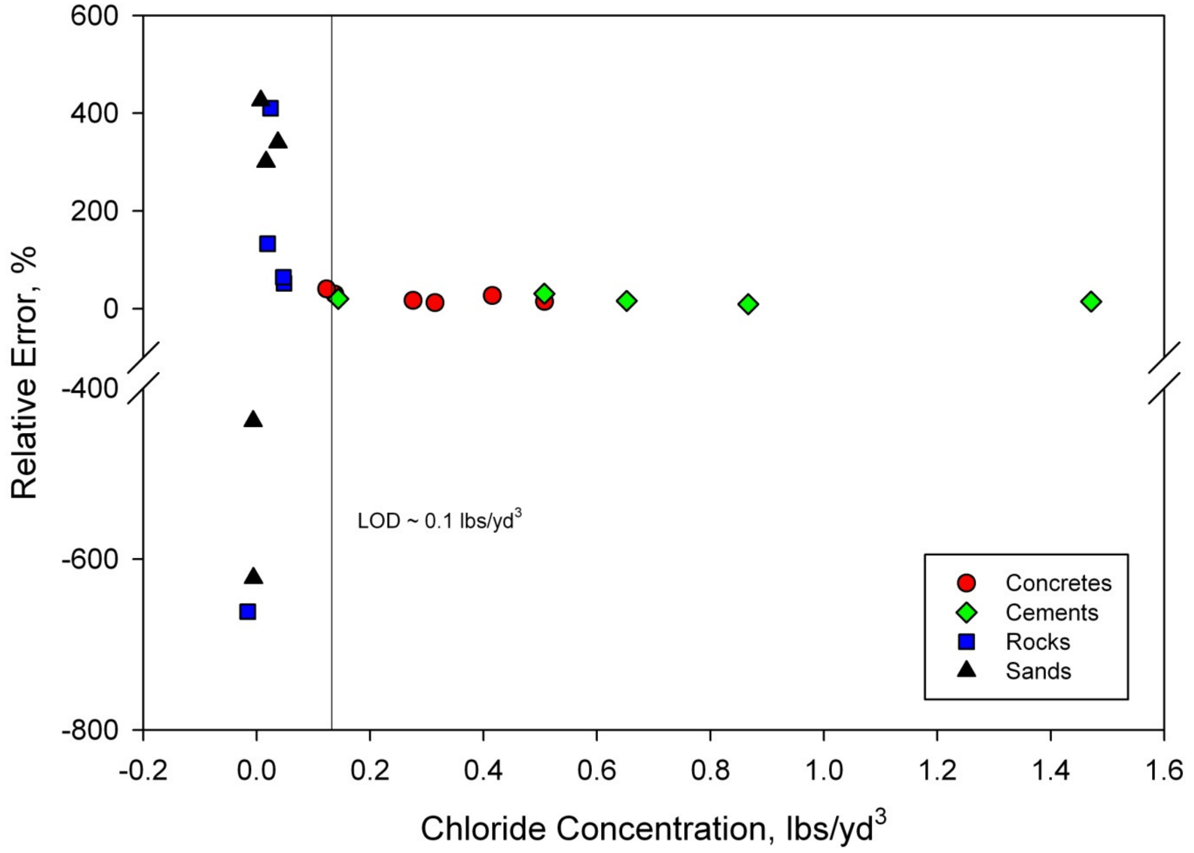

Figure 6-1. Relative error RE% versus chloride concentration in concrete and coarse and fine aggregates.

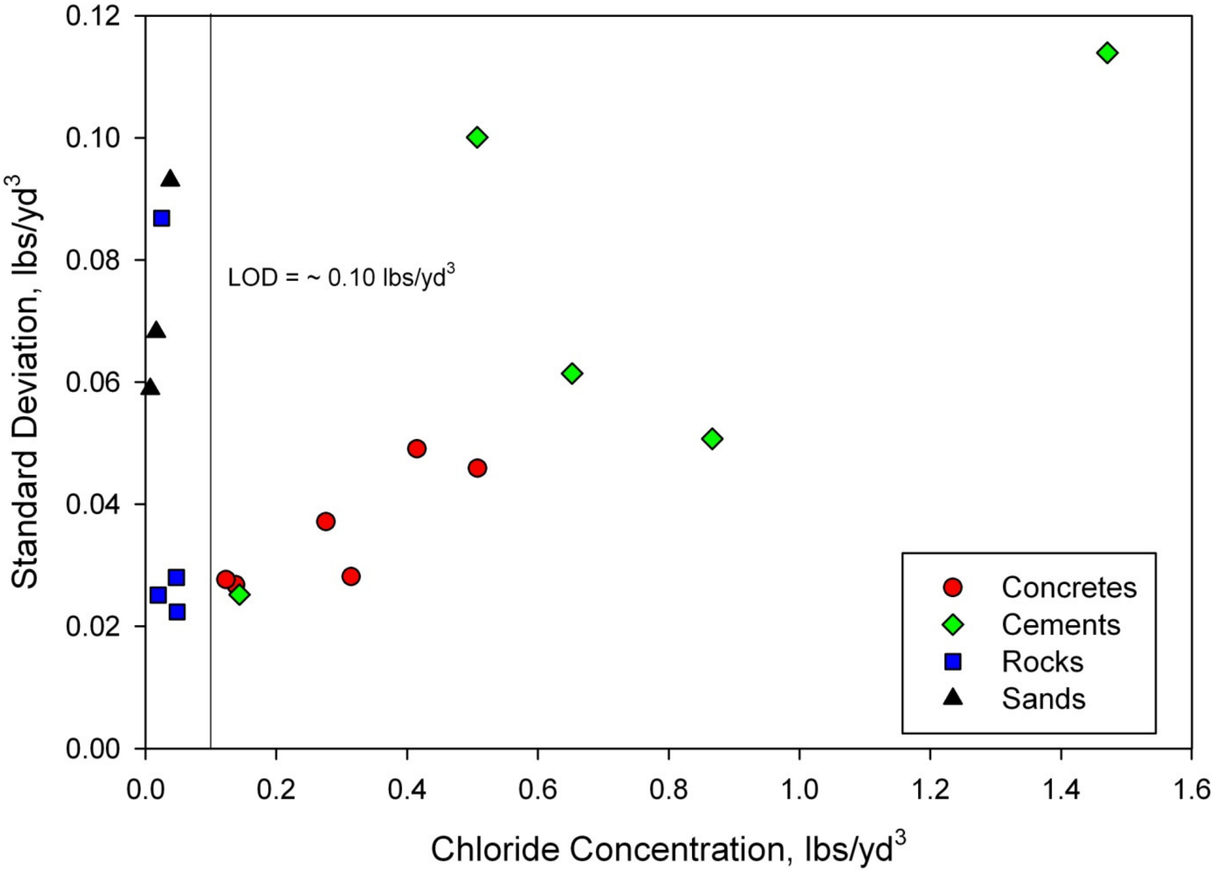

Figure 6-2. Standard deviation s_r versus chloride concentration in concrete and coarse and fine aggregates.

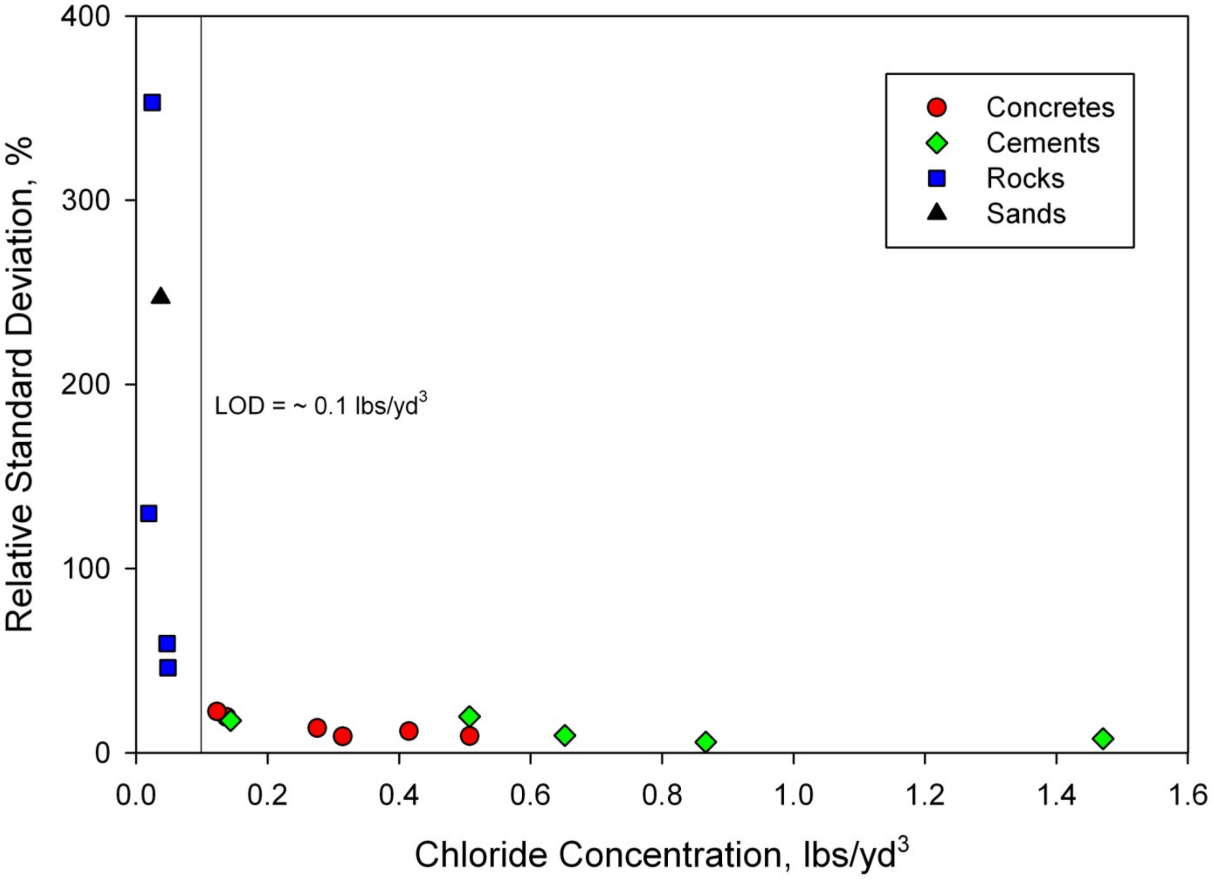

Figure 6-3. Relative standard deviation RSD% or CV versus chloride concentration in concrete and coarse and fine aggregates.

Figure 6-4 plots the standard deviation versus chloride content for concretes 4470, 4471, 4472, 4473, 4474, 062, and within-laboratory standard deviation for 1-B and 2-A from Section 10, Table 10-7. Equation 6-8 is a linear model (r = 0.86) applied to the data set, where s_r is the within-laboratory standard deviation of chloride concentration for concentration C_{Cl} (lbs/yd^3).

$$s_r = 0.0183 + 0.0561 \cdot C_{Cl} \tag{6-8}$$

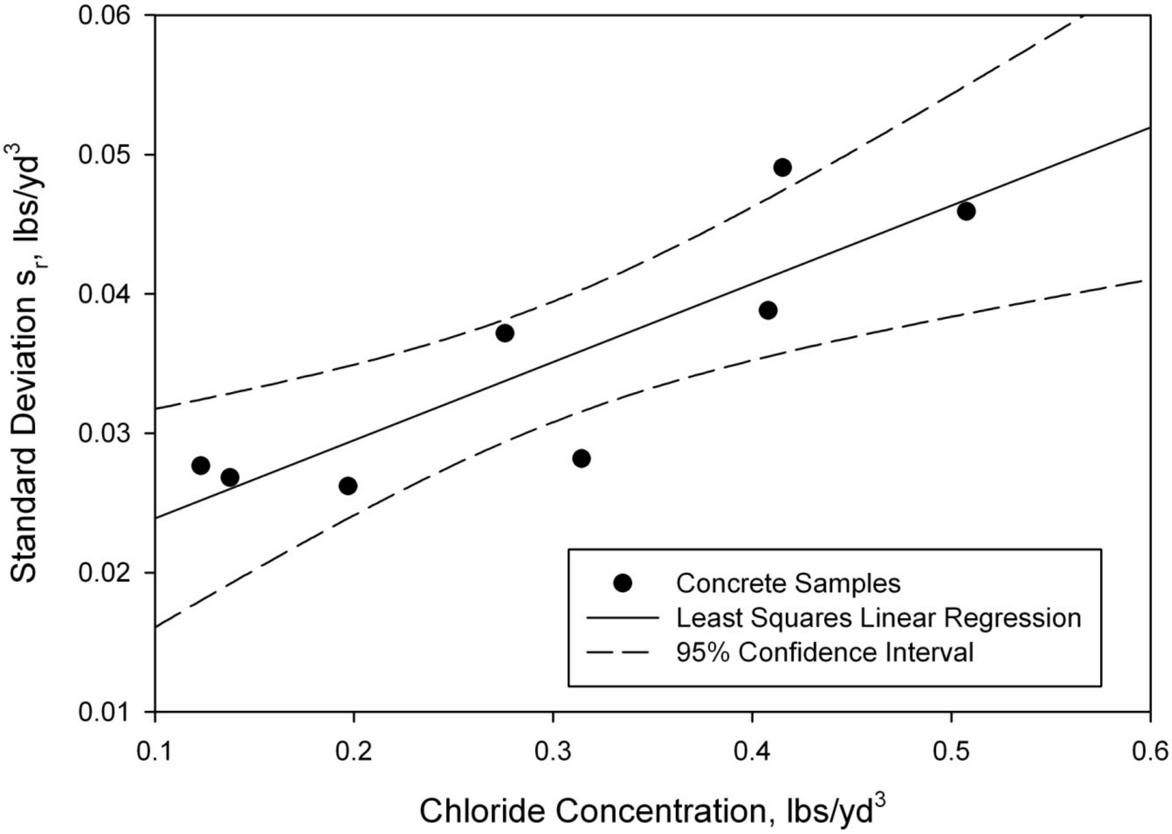

Figure 6-4. Standard deviation of chloride concentration versus chloride concentration for concrete.

6.3 Analysis of a Standard Reference Material

A standard reference material SRM 1880b Portland Cement was obtained from National Institute of Standards and Technology (NIST) to serve as an independent reference material (see Appendix B for definition) to validate the method accuracy and precision. According to the Certificate of Analysis, SRM 1880b had a chloride content of 0.01830 ± 0.00057% (mass fraction), which was determined by X-ray fluorescent spectrometry with standard additions at NIST and ion-selective electrode at a collaborating laboratory.

Eight chloride determinations were made of SRM 1880b: three with a silver/sulfide electrode and five with a chloride electrode and all on the same day, however, the electrodes were assigned in random order. Hypothesis testing at the 95% significant level revealed that based on a two-tailed t-test ($p = 0.68$) and an F-test ($p = 0.47$) the averages and standard deviations of chloride titration end points between silver/sulfide and chloride electrode measurements were not different. Descriptive statistics for the pooled data are shown in Table 6-1.

Table 6-1 Descriptive Statistics of Titration End Points for NIST SRM (units in mL)

Statistic	SRM 1880b
Mean	1.631
Standard Error	0.009
Median	1.639
Mode	NA
Standard Deviation	0.027
Sample Variance	0.001
Kurtosis	-0.679
Skewness	-0.895
Range	0.066
Minimum	1.592
Maximum	1.658
Sum	13.052
Count	8
Confidence Level (95.0%)	0.021

The average chloride concentration ± standard deviation found for NIST SRM 1880b, expressed as a mass fraction, were 0.01890 ± 0.00046 %, when corrected for a blank using Equations 2-2 and 4-5, respectively (refer to Table 4-2 blank statistics). No significant difference was found between this chloride mass fraction and that reported by NIST based on a one-tailed t-test at the 95 % confidence level. The relative error (Equation 6-3) and relative standard deviation were -3.27 % and 2.43 %, respectively.

6.4 Analysis of FDOT Laboratory Control Sample

As part of this study, FDOT supplied laboratory control samples LCS (see Appendix B for definition) to check method accuracy and precision. These control samples were identified as concretes 4470, 4471, 4472, 4473, and 4474; 4470 had no added chloride and served as a baseline for correcting the total chloride content to the target chloride concentration. Refer to Table 6-2 for a summary of results.

Table 6-2 Summary of Chloride Concentrations Measured in FDOT Laboratory Control Samples (units in lbs/yd^3)

Sample ID	4470	4471	4472	4473	4474
Target	Background	0.115	0.172	0.23	0.287
Avg	0.151	0.291	0.329	0.430	0.523
StDev	0.023	0.035	0.025	0.047	0.044
RSD*	15.1%	11.9%	7.5%	11.0%	8.4%
Less Bckgd	-	0.140	0.178	0.279	0.372
RE**	-	21.6%	3.7%	21.4%	29.5%

*Equation 6-7; **Equation 6-3

Unlike the small relative error found for NIST SRM 1880b Portland cement (see Section 6-3), relative errors for the LCS were found to be as high as ~30% (Table 6-2). Some of the observed error was likely due to differences in sample extract pH: ~pH 8 for cement and ~pH 1.5 for LCS, because the electrode response changes outside the range of pH 2-12 (section 5). For samples extracts below pH 2, the more acidic the extract the more titrant is required to complete the titration. This means that if the titrant normality or delivery volume has even a small error, the error accumulates over the course of the titration and affects the slope obtained from a linear model applied to a plot of Gran function F versus cumulative volume (Equation 2-1).

For the results shown in Table 6-4, 0.01 N silver nitrate was pipetted in 0.5 mL aliquots from a 5-mL repipet II dispenser (Thermo Scientific). For these data, delivery volume was calibrated to a 1-mL line on a 10-mL graduated cylinder, a line that was checked by weighing to 0.1 mg the mass of water that would make 1 mL of water at room temperature. On the suspicion that this calibration technique was not precise enough, the technique was modified to replace the graduated cylinder with a 5-mL volumetric flask to which ten 0.5 mL aliquots were added. As before, the 5-mL mark was checked with an appropriate mass of water. The repipet II dispenser could neither be adjusted properly nor operated consistently enough to deliver 5 mL in this manner; however, the delivery was improved enough to merit re-analyzing the LCS samples in triplicate (Table 6-3). Re-analysis was done using a silver/sulfide electrode.

Table 6-3 Summary of Chloride Concentrations Measured in FDOT Laboratory Control Samples after Implementing New Calibration Technique (units in lbs/yd^3)

Sample ID	4470	4471	4472	4473	4474
Target	Background	0.115	0.172	0.23	0.287
Avg	0.134	0.245	0.314	0.398	0.495
StDev	0.027	0.035	0.031	0.037	0.020
RSD*	8.36%	6.25%	4.40%	4.17%	1.78%
Less Bckgd		0.107	0.180	0.263	0.361
RE**		-6.64%	4.71%	14.5%	25.6%

*Equation 6-7; **Equation 6-3

Note in Table 6-3 the unambiguous trend in relative error, which increased with chloride content and suggests that further improvement in the titration delivery volume is needed to reduce the error at higher chloride concentrations.

6.5 Analysis of Error

To diagnose systematic and random errors associated with the potentiometric measurements, a chloride check standard prepared at 3.00 mg/L (ppm), an amount of chloride equivalent to chloride content in concrete of ~0.40 lbs/yd^3, was routinely analyzed. Refer to Table 6-4 for the descriptive statistics.

Table 6-4 Descriptive Statistics for Titration End Points of a 3 ppm Chloride Standard Measured Using a Silver/Sulfide Electrode (units in mL)

Statistic	Chloride
Mean	0.870
Standard Error	0.010
Median	0.871
Mode	NA
Standard Deviation	0.044
Sample Variance	0.002
Kurtosis	-0.124
Skewness	-0.336
Range	0.171
Minimum	0.773
Maximum	0.944
Sum	15.663
Count	18
Confidence Level (95.0%)	0.022

The average blank-corrected chloride concentration was 2.94 ppm; the relative error (Equation 6-3) and relative standard deviation (Equation 6-7) were -2.03 % and 1.68 %, respectively. The relative error and relative standard deviation were smaller than but otherwise consistent with those seen for NIST SRM 1880b Portland cement.

Ellison et al. (2009) recommend a spreadsheet calculation to examine combined uncertainty for checking a reference material. The value and uncertainty of each of the measured parameters (p, q, r, s) in Equation 2-2 were included for this approach. A spreadsheet 4 x 4 matrix representing rows p through s and columns p through s was prepared: in row p, column p, the value p was incremented by its uncertainty; all other cells in row p contained the value of p. This was repeated in row q with value q through row s with value s. In each column p, q, r, and s the chloride concentration was calculated according to Equation 2-2 from entries in the column's cells; the column chloride concentration was then subtracted from the average chloride concentration. Taking the square root of the sum of squares for the cells containing these differences yields the combined uncertainty. The spreadsheet matrix is shown in Table 6-5. With this approach one can examine the effects of a parameter or parameter uncertainty change on the combined uncertainty.

Table 6-5 Spreadsheet Approach to Calculating Combined Uncertainty

Parameter	Average	Standard Error	Letter	p	q	r	s
Blank end point, mL	0.0328	0.0042	p	0.0370	0.0328	0.0328	0.0328
Standard end point, mL	0.8701	0.0104	q	0.8701	0.8806	0.8701	0.8701
Titrant normality, N	0.0100	0.0001	r	0.0100	0.0100	0.0101	0.0100
Sample volume, mL	101.0	0.1000	s	101.0	101.0	101.0	101.1
Concentration, ppm	2.939	-	-	2.924	2.976	2.969	2.936
Differences	-	-	-	-0.014	0.037	0.029	-0.003
Combined uncertainty, ppm	0.049	-	-	-	-	-	-

Note that for this approach relative uncertainty is 1.67 %, which is consistent with the observed value of 1.68 %. Standard titration end point and titrant normality contributed the most to the combined uncertainty shown in Table 6-5 and emphasizes the importance of maintaining accurate titrant normality and delivery volumes.

According to electrode manufacturer, under controlled conditions silver (Thermo, 2007) or chloride (Thermo, 2003) measurements are reproducible within ± 2 %. Uncertainty estimates from replicate analyses of a NIST SRM and a chloride check standard spanned this reproducibility.

6.6 Significant Figures for the Chloride Results

Significant figures in a number are all of the certain digits and the first uncertain digit (Skoog et al., 1996), and approach that works best when figures are presented in scientific notation, as there is no question about whether a zero as either a placeholder or a significant figure (for example, in the numbers 1,000 mL or 0.0010 L). Current convention is to carry at least one digit beyond the uncertain digit through all of calculations to avoid rounding errors (Skoog et al., 1996). An extra digit on tabulated results such as those found in a report table such as Table 7-4 allows data re-analysis at a later date.

Precision for FM 5-516 was dependent both on chloride content and matrix, but for chloride content in hardened concrete between the LOD 0.10 (± 0.02) lbs/yd^3 (Table 7-5) and compliance limit of 0.40 (± 0.05) lbs/yd^3 (Table 10-5), the final results should be presented with no fewer than two digits. Chloride computational results in FM 5-516 software should be saved with at least four digits and presented to the operator with no less than 3 digits, as further data aggregation or analyses are likely.

6.7 Summary of Results

Below a chloride content of ~0.10 lbs/yd^3 in hardened concrete and aggregates, accuracy and precision of FM 5-516 rapidly degraded. Above this chloride content, repeatability standard deviation s_r increased but RSD% (or CV) decreased with increasing chloride content over the range of content studied.

Accuracy and precision estimates for a 3.00 ppm chloride calibration standard titrated according to FM 5-516 were -2.03 % and 1.68 %, respectively; and these results were consistent with an error analysis that yielded a combined uncertainty of 1.67 % for such a standard. Thus, routine laboratory measurements of a 3.00 ppm chloride check standard should be within ± 5 % if the method is under control,

Accuracy and precision estimates for a 183-ppm (1.00 lbs/yd^3) NIST SRM 1880b Portland cement extracted and analyzed according to FM 5-516 were -3.27 % and 2.43 %, respectively, in contrast to estimates of 25.6 % and 1.78 % for LCS concrete 4474 (Table 6-3). The suspected cause of the large systematic error seen for concrete 4474 is the inaccuracy of the titrant delivery system in combination with an acidic sample extract.

It is recommended that a future version of FM 5-516:

- Increase the mass of pulverized hardened concrete that is extracted for chloride such that the final extract has pH > 2 and decrease the mass of powdered cement such that the final extract has pH < 8;

- Require the addition of a cement LCS to pulverized non-alkaline samples such as rock or sand such that the resulting extract has pH > 2; and
- Specify the tolerance of the titrant delivery system and require daily checks of titrant delivery volume accuracy using at least 10 cumulative 0.5-mL volumes.

7 Sensitivity of Method Factors to Perturbation

7.1 Overview

Many factors influence the measurement of chloride concentration in powdered concrete samples. These factors include but are not limited to:

- Operator;
- Choice of electrode;
- Size distribution of powdered concrete;
- Temperature;
- Mass, volume, and voltage measurements;
- Mass transfers;
- Sources of contamination or interference; and
- Chloride concentration.

Many of these factors can be more or less controlled in the laboratory by standard laboratory practice, equipment specification, or method procedures, while other factors such as interference or chloride content may not be under the control of the laboratory. The purpose of this sensitivity study was to assess which, if any, method factors need better control to achieve the desired method performance across laboratories.

7.2 Results for Concrete 4473

A sensitivity test of FM 5-516 was performed on FDOT concrete 4473; factors and the corresponding conditions were chosen based the experiences of one operator after ~400 analyses with the method. Each experiment was run as a batch with a total of nine analyses: one deionized water blank and eight replicates. Placement of sample extracts on the hot plate and the sequence in which extracts were analyzed were randomized to reduce systematic error. The electrode filling solution was flushed out and refilled on the combination electrode and sensing surface was polished between each experiment. In each experiment four replicates represented the unchanged method and four replicates represented a small change to the method as shown in Table 7-1.

Table 7-1 List of Factors and Conditions for Concrete 4473

Factor Number	Factor Letter	Condition	Value for Capital Letter (Unchanged)	Value for Lower Case Letter (Changed)
1	A, a	Sample mass	3.0 g	3.3 g
2	B, b	Acid strength	1.1 N	0.9 N
3	C, c	Electrode	Silver	Chloride
4	D, d	Acid boiling time	3 mins	5 mins
5	E, e	Acid volume	35 mL	30 mL
6	F, f	Titrant strength	0.01 N	0.0125 N
7	G, g	Titration timing	>1.5 hrs	<1.5 hrs

A box plot was prepared to display graphically the percentile distribution of data for each experiment and condition (Figure 7-1). The overall average and median chloride concentrations were 0.414 lbs/yd^3 and 0.417 lbs/yd^3, respectively. A Student's t-test was applied to test the hypothesis that the means of chloride concentrations for the two conditions within an experiment were not significantly different (Table 7-2). An F-test was applied to test the hypothesis that the variances of chloride concentrations for the two conditions within an experiment were not significantly different (Table 7-2).

Table 7-2 Hypothesis Testing of Factors and Conditions for Concrete 4473

Factor	1	2	3	4	5	6	7
t-test p*	0.026	0.063	0.357	0.942	0.908	0.000	0.040
F-test p*	0.272	0.621	0.475	0.472	0.015	0.037	0.151

*Probability of a type I error

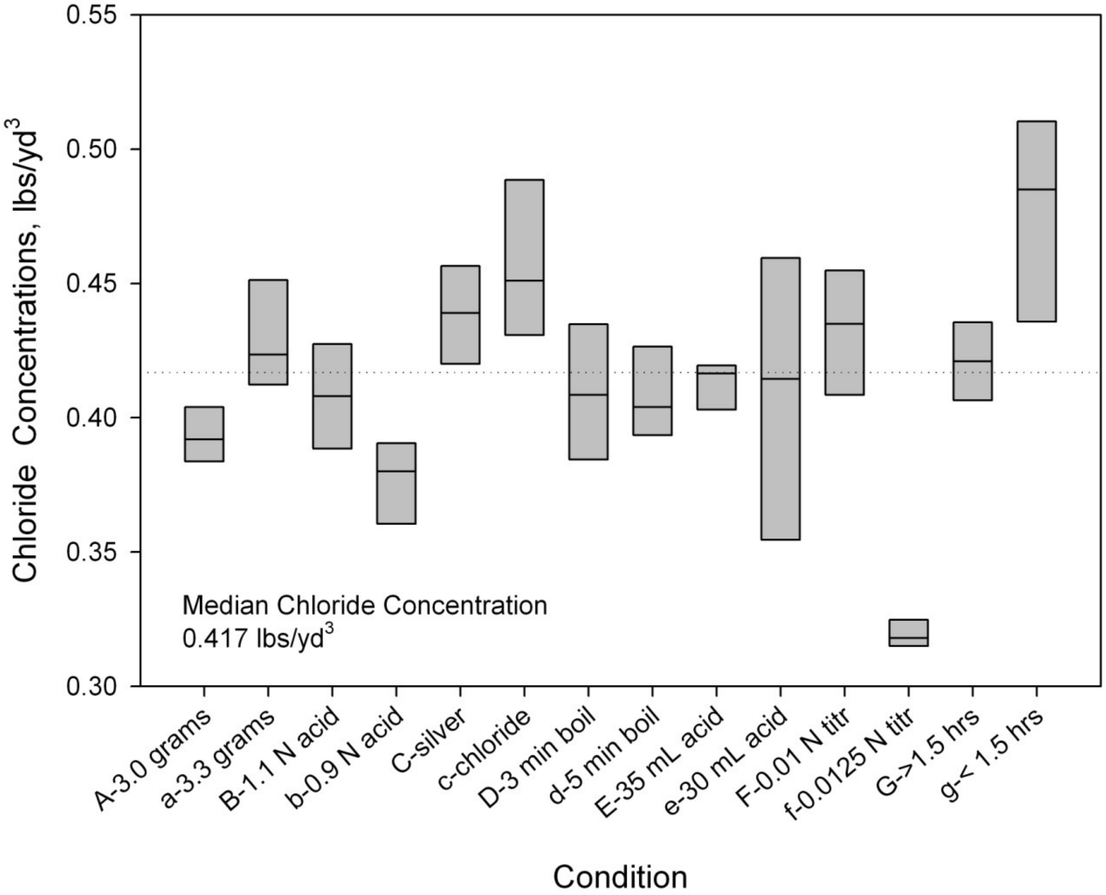

Figure 7-1. Box plot of sample chloride concentration versus experimental condition for FDOT concrete 4473. Solid lines for each box represent the 25%, 50%, and 75% percentiles based on four replicates per condition.

A two-tailed Student's t-test revealed that average chloride concentration for two conditions examined in Factors 1, 6, and 7 were significantly different at the 95% confidence level; and an F-test revealed that chloride concentration variances for the two conditions examined in Factors 5 and 6 were significantly different at the 95% confidence level.

For Factor 1, a 10 % increase in sample mass had a significant effect on measured chloride content in concrete 4473 extracts. Such a gain (or loss) in sample mass could occur if a sample container was not properly tared between mass measurements. A taring error can be avoided by using a single pre-weighed watch glass so that the final sample plus watch glass mass is always the same; moreover, this approach would serve as a continuous check of analytical balance calibration.

Another way for a sample to change mass is by absorbing moisture from the atmosphere. Under these conditions, a wet 3-g sample has less chloride content than a corresponding dry 3-g sample, as less of the weight is actually sample. The version of FM 5-516 included in Kessler et al. (1978) included a step for drying the sample for four hours at 105 ^{o}C between sample storage and analysis. The 2005 version of FM 5-516 has a step for drying crushed concrete samples two to four hours at 110 ^{o}C prior to pulverizing, a step that prevents the powder from sticking to machine surfaces. For comparison, NIST Standard Reference Material 1880b Portland Cement recommends that if stored after opening, mass of cement samples should be corrected for moisture or carbonate loss on ignition (LOI) at 950 ^{o}C per ASTM C114. Moisture content of concrete and aggregate materials used for this study were determined by drying stored samples in an oven at 105 ^{o}C for two hours and calculating the percent change between the pre- and post-weighed sample mass. Average moisture contents were 0.45% for cement, 0.11% for concrete, 0.06% for sand, and 0.05% for rock samples received for this study, well below the 10 % used for the sensitivity analysis.

For Factor 5, a 5-mL decrease in the amount of acid had a significant effect on the variance of measured chloride content in concrete 4473 extracts, possibly a consequence of shifting the sample extract pH within the range where the electrode response changes. Kessler et al. (1978) noted that higher chloride contents were measured when the sample extract was below ~pH 2 and though not statistically significant ($p = 0.06$); this effect can be seen for Factor 2 as well.

For Factor 6, a 25 % increase in the titrant strength significantly decreased measured chloride content in concrete 4473 extracts. This result illustrates the importance of maintaining control not only of the titrant concentration but on its delivery volume. Silver nitrate solutions degrade upon exposure to light and per FM 5-516 should be stored in the dark. Water in silver nitrate can evaporate over time concentrating the titrant, more so when titrant is stored with headspace and in bottles that are not airtight. A working solution of 0.01 N silver nitrate should be prepared fresh each week and its chloride concentration assured by daily titration against a chloride calibration standard. Delivery volume should be checked daily with a minimum of 10 sequential 0.5-mL volumes, for example, in a 5-mL volumetric flask, to assure the titrant dispensing operation is under control.

For Factor 7, a longer cool-down time of sample extracts significantly decreased measured chloride content in concrete 4473 extracts. Per FM 5-516, sample extracts should reach room temperature before they are analyzed, which is usually achieved within ~1.5 hrs of filtration. Another explanation borne out by later testing is that over time the electrode response changes as contaminants in sample extracts coat the electrode membrane surface. Cleaning and conditioning the electrode between sample batches is recommended.

7.3 Results for Concrete 062

A sensitivity test of FM 5-516 was performed on FDOT concrete 062; factors and the corresponding conditions were chosen based the experiences of one operator after ~500 analyses with the method and so as not to repeat the conditions used for concrete 062. Each experiment was run as a batch with a total of nine analyses: one de-ionized water blank and eight replicates. Placement of sample extracts on the hot plate and the sequence in which extracts were analyzed were randomized to reduce systematic errors. The electrode filling solution was flushed out and refilled on the combination electrode and sensing surface was polished between each experiment. In each experiment four replicates represented the unchanged method and four replicates represented a small change to the method as shown in Table 7-3.

Table 7-3 List of Factors and Conditions for Concrete 062

Factor Number	Factor Letter	Condition	Value for Capital Letter (Unchanged)	Value for Lower Case Letter (Changed)
1	A, a	Titrant delivery	Pipettor	Burette
2	B, b	Ionic strength	No ISA	ISA added
3	C, c	Voltmeter	XL60	IA255
4	D, d	Acid storage	Headspace	No headspace
5	E, e	Stirring rate	Moderate	High
6	F, f	Rinse water temp	Warm	Cool
7	G, g	Electrode slope	25.19	25.71

For this concrete, the amount of pulverized sample was sufficient for the first six of seven experiments (Factors 1 through 6). For the seventh experiment, four measurements were randomly selected from 24 measurements that represented the unchanged condition. For the changed condition, the chloride concentration for each of these methods was re-computed with modified Chloride 2008 software using the theoretical electrode slope for an ambient temperature of 25 ^{o}C.

A box plot was prepared to display graphically the percentile distribution of data for each experiment and condition (Figure 7-2). The overall average and median chloride concentrations were 0.119 lbs/yd^3 and 0.116 lbs/yd^3, respectively. A Student's two-sided t-test was applied to test the hypothesis that the means of chloride content for two factor conditions within an experiment were not significantly different (Table 7-4). An F-test was applied to test the hypothesis that the variances of chloride content for the two factor conditions within an experiment were not significantly different (Table 7-4).

Table 7-4 Hypothesis Testing of Factors and Conditions for Concrete 4473

Factor	1	2	3	4	5	6	7
t-test p*	0.611	0.687	0.288	0.785	0.021	0.456	0.779
F-test p*	0.999	0.352	0.904	0.706	0.336	0.809	0.966

*Probability of a type I error

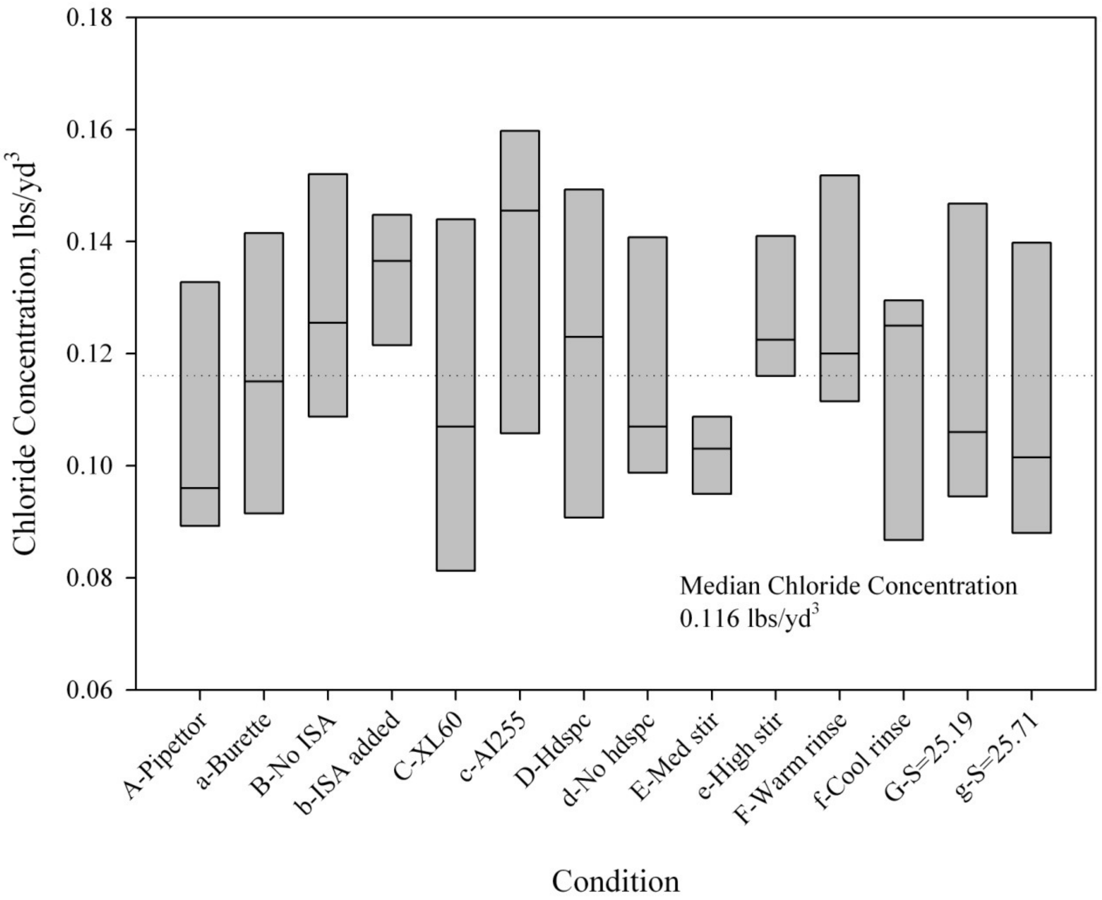

Figure 7-2. Box plot of sample chloride concentration versus experimental condition for FDOT concrete 4473. Solid lines for each box represent the 25%, 50%, and 75% percentiles based on four replicates.

No factor had a significantly different variance between its two imposed conditions.

For Factor 5, a higher stirring rate yielded significantly different chloride content for concrete 062 extracts. For the silver/sulfide electrode a higher stirring rate caused the electrode reading to stabilize quicker, especially close to the titration end point. Although layers of cardboard separated the stirred beaker from the metal surface of the stirring apparatus, the higher stirring rate could have caused a marginal increase in the temperature of the extract and thus increased the Nernstian slope of the electrode. It is recommended that FM 5-516 require that stirring rate not only be set mid-range and but held constant throughout the test. A warm-up period may be required on some equipment to obtain a steady-state stirring speed.

7.4 Simulated Inter-Laboratory Study

Data acquired for testing the sensitivity of FM 5-516 to changes in method factor conditions can be used to simulate an inter-laboratory study. If data are tabulated as shown in Table 7-5, where each column represents one laboratory and each row of a column represents one replicate, then each column has a unique set of factor perturbations and in that respect is realistic of what might be found in an actual inter-laboratory study (Youden, 1975). Results for concrete 4473 and concrete 062 are presented in Tables 7-6 and 7-7.

Table 7-5 Data Organization for a Simulated Inter-Laboratory Study

	Simulated Laboratory							
Factor	1	2	3	4	5	6	7	8
A or a	A	A	A	A	a	a	a	a
B or b	B	B	b	b	B	B	b	b
C or c	C	c	C	c	C	c	C	c
D or d	D	D	d	d	d	d	D	D
E or e	E	e	E	e	e	E	e	E
F or f	F	f	f	F	F	f	f	F
G or g	G	g	g	G	g	G	G	G

Table 7-6 Chloride Content of FDOT Concrete 4473 Using FM 5-516 (arranged according to Table 7-1; units are lbs/yd^3)

	Simulated Laboratory							
Factor	1	2	3	4	5	6	7	8
1	0.386	0.398	0.406	0.383	0.422	0.409	0.460	0.425
2	0.388	0.426	0.377	0.355	0.428	0.390	0.393	0.383
3	0.414	0.499	0.438	0.426	0.44	0.445	0.462	0.457
4	0.384	0.431	0.395	0.431	0.413	0.393	0.386	0.436
5	0.415	0.461	0.42	0.374	0.455	0.399	0.348	0.418
6	0.403	0.318	0.327	0.445	0.425	0.314	0.318	0.458
7	0.437	0.516	0.477	0.431	0.493	0.405	0.411	0.422

Table 7-7 Chloride Content of FDOT Concrete 062 Using FM 5-516 (arranged according to Table 7-1; units are lbs/yd^3)

	Simulated Laboratory							
Factor	1	2	3	4	5	6	7	8
1	0.096	0.087	0.096	0.145	0.119	0.111	0.149	0.085
2	0.157	0.137	0.119	0.129	0.107	0.114	0.145	0.144
3	0.075	0.144	0.100	0.093	0.114	0.164	0.154	0.147
4	0.084	0.135	0.113	0.098	0.101	0.150	0.111	0.154
5	0.094	0.115	0.098	0.126	0.119	0.109	0.146	0.108
6	0.124	0.125	0.131	0.110	0.116	0.074	0.125	0.161
7	0.096	0.094	0.150	0.157	0.086	0.094	0.116	0.109

Refer Sections 10-2 and 10-3 for an explanation of the steps in processing and interpreting results of an inter-laboratory study.

For concrete 4473 (Table 7-6), data were normally distributed with no individual outliers based on a Kolmogorov-Smirnov (K-S) test (Ellison et al., 2009) and a Student’s t-test, respectively, at the 99% confidence level. Levene’s test for homogeneity of variance was not significant at the 99% confidence level (variances were homogeneous). Using ANOVA, no significant differences were seen between mean chloride content from simulated laboratories when tested at the 99 % confidence level. Components of variance, variances, standard deviations, and coefficients of variations (Tables 7-8 and 7-9) were obtained from ANOVA.

For concrete 062 (Table 7-7), data were *not* normally distributed based on a Kolmogorov-Smirnov (K-S) test; however, a normal probability plot of group mean residuals gave a straight line, indicating that the departure from normality was not likely serious. The consequences of analyzing data that do not have normal distribution with statistics that assume normality is that calculated p values are not true p values (Ellison et al., 2009).

A Student’s t-test revealed no individual outliers at the 95 % and 99 % confidence level and Levene’s test for homogeneity of variance was not significant at the 95 % and 99 % confidence level (variances were homogeneous). Using ANOVA, no significant differences were seen between mean chloride content from simulated laboratories when tested at the 95 % and 99 % confidence level. Components of variance, variances, standard deviations, and coefficients of variations (Tables 7-8 and 7-9) were obtained from ANOVA.

Table 7-8 Averages, Components of Variances, and Variances for Simulated Inter-Laboratory Study (units are lbs/yd^3)

Concrete	Averages	Components of Variance		Variances	
		Within Labs	Between Labs	Within Labs	Between Labs
062	0.119	0.000558	2.67E-05	0.000558	0.000585
4473	0.414	0.001761	7.12E-05	0.001761	0.001833

Table 7-9 Averages, Standard Deviations, and Coefficients of Variation for Simulated Inter-Laboratory Study (units are lbs/yd^3)

Concrete	Averages	Standard Deviations		Coefficients of Variation	
		Within Labs	Between Labs	Within Labs	Between Labs
062	0.119	0.0236	0.0242	19.9	20.4
4473	0.414	0.0420	0.0428	10.2	10.4

As chloride content in concrete increased, standard deviations increased but coefficients of variation decreased (Table 7-6), a trend seen by Kessler et al. (1982) as well as in this study (Section 6-2). The maximum allowable range for a single operator who tests three replicates of a pulverized hardened concrete is CI_r, where CI_r is the 95 % confidence interval and s_r is the within-laboratory standard deviation at the nominal chloride content (Equation 7-1; ASTM C670, 2003).

$$CI_r = 3.3 \cdot s_r \tag{7-1}$$

From this simulated inter-laboratory study, the maximum allowable range calculated for a hardened concrete with a nominal chloride content of 0.40 lbs/yd^3 was 0.14 lbs/yd^3, which is greater than the value of 0.080 lbs/yd^3 estimated by Kessler et al. (1982) and specified by FM 5-516.

The simulated inter-laboratory study showed that the within-laboratory component of variance was greater than the between-laboratory component (Table 7-5), which might well be the case for an actual study if other laboratories do not follow the same procedures for reasons such as ambiguous instructions or undefined environmental factors, and both random and systematic error vary between laboratories (Youden, 1975; see Section 6.1 for discussion). Proposed revisions to FM 5-516 (Section 8; Appendix D) are intended to reduce the within-laboratory component of variance.

7.5 Electrode Comparisons

Chloride determinations were made according to FM 5-516 with both combination chloride electrode and combination silver/sulfide electrode for cement, concrete, rock, and sand samples to test the hypotheses that neither average chloride content nor variance of chloride content was different between electrodes. Hypotheses testing were one with a two-sided Student's t-test and an F-test, both at the 95 % confidence level, and results are shown in Table 7-7. Chloride concentrations in rock and sand were below the LOD (Section 6-2) and so were not included.

Table 7-10 Results of Hypothesis Testing for Electrode Comparisons

Statistic	40	41	42	43	Argos	4470	4471	4472	4473	4474	1 ppm Cl	Blank
t-test	0.503	0.436	0.284	0.257	0.751	0.143	0.018	0.066	0.992	0.098	0.551	0.342
F-test	0.831	0.382	0.634	0.625	0.949	0.616	0.976	0.668	0.463	0.428	0.619	0.959
N, chloride*	3	4	3	2	3	3	3	3	3	3	5	7
N, silver*	3	2	3	4	3	3	3	3	3	3	5	8

*Electrode

These results indicate that there is not enough evidence to reject either hypothesis. Both the combination chloride electrode and the combination silver/sulfide electrode yielded the same chloride concentrations when chloride content in cement and concrete within a range of 0.10 lbs/yd^3 to 1.00 lbs/yd^3 was determined with FM 5-516. Consequently, there is no compelling reason for FM 5-516 to exclude these electrodes.

7.6 Summary of Results

Sensitivity of FM 5-516 to perturbation in method factors was explored for concretes 4473 and 062, with average chloride contents of 0.414 lbs/yd^3 and 0.119 lbs/yd^3, respectively. Hypothesis testing of replicated results of small changes in individual factors revealed that errors in sample weight, titrant concentration, titrant delivery volume, stirring rate, or amount of added acid, as examples, significantly affected either the measured chloride content or its standard deviation, or both. Simulations of inter-laboratory study data for each of these concretes were reasonably consistent with results from an earlier study by Kessler et al. (1982), except that the maximum allowable range calculated for concrete 4473 was 0.14 lbs/yd^3, which is greater than the value of 0.080 lbs/yd^3 estimated by Kessler et al. (1982) for a concrete of similar chloride content. Proposed revisions to FM 5-516 seek reductions in sources of variability with high leverage such as titrant delivery volume.

8 Trend Analysis

Trend analysis can be applied to routine measurements as a way to track and quantify method performance in such measures as accuracy, precision, and limit of detection (LOD). One approach is to plot over time either single measurements such as daily blank measurements or the difference between duplicate measurements and define on these plots upper and lower control limits that serve as “warning” or “action” limits (ASTM D3856, 2006; Ellison et al., 2009).

One tool for trending sequential data is a Shewhart chart, as shown in Figure 8-1. Features of this Shewhart chart include a center line that represents the mean of all observations, a pooled standard deviation (Equation 8-1), and upper and lower control limits (UCL, LCL) set at 3.0 σ (Ellison et al., 2009) or 3.27 σ (ASTM D3856, 2006); the latter corresponds to a probability that one observation in 1,000 will by chance fall outside these limits. In a Shewhart chart, dates are treated as categorical variables. For routine duplicate measurements, the corresponding Shewhart chart is constructed with difference versus date and the average and standard deviation of differences are used for center line and control limits, respectively.

For the example shown in Figure 8-1, some days had more than one blank measurement. In this case, a pooled standard deviation s_p is calculated according to Equation 8-1, where N_1 is the number of observations and $\bar{x}_1$ is the mean of the observations for the first data set, N_2 is the number of observations and $\bar{x}_2$ is the mean of the observations for the second data set, and so forth, and N_t is the total number of data sets.

$$s_p = \sqrt{\frac{\sum_{i=1}^{N_1}(x_i-\bar{x}_1)^2+\sum_{j=1}^{N_2}\left(x_j-\bar{x}_2\right)^2+\sum_{k=1}^{N_3}(x_k-\bar{x}_3)^2+\cdots}{N_1+N_2+N_3+\cdots-N_t}} = \sqrt{\frac{(N_1-1)s_1^2+(N_2-1)s_2^2+\cdots(N_t-1)s_t^2}{(N_1-1)+(N_2-1)+\cdots(N_t-1)}} \qquad (8\text{-}1)$$

According to Ellison et al. (2009) data trends that also signal a change in method performance include

- Two successive data points outside of 2 σ (2 σ is not shown on Figure 8-1);
- Nine successive data points on the same side of the mean; or
- Six successive data points steadily increasing or decreasing.

For the data plotted in Figure 8-1, three points were outside the control limits, which suggest that although all of these observations were within -0.10 to +0.10 mL as required by FM5-516, on at least three days the method was out of control.

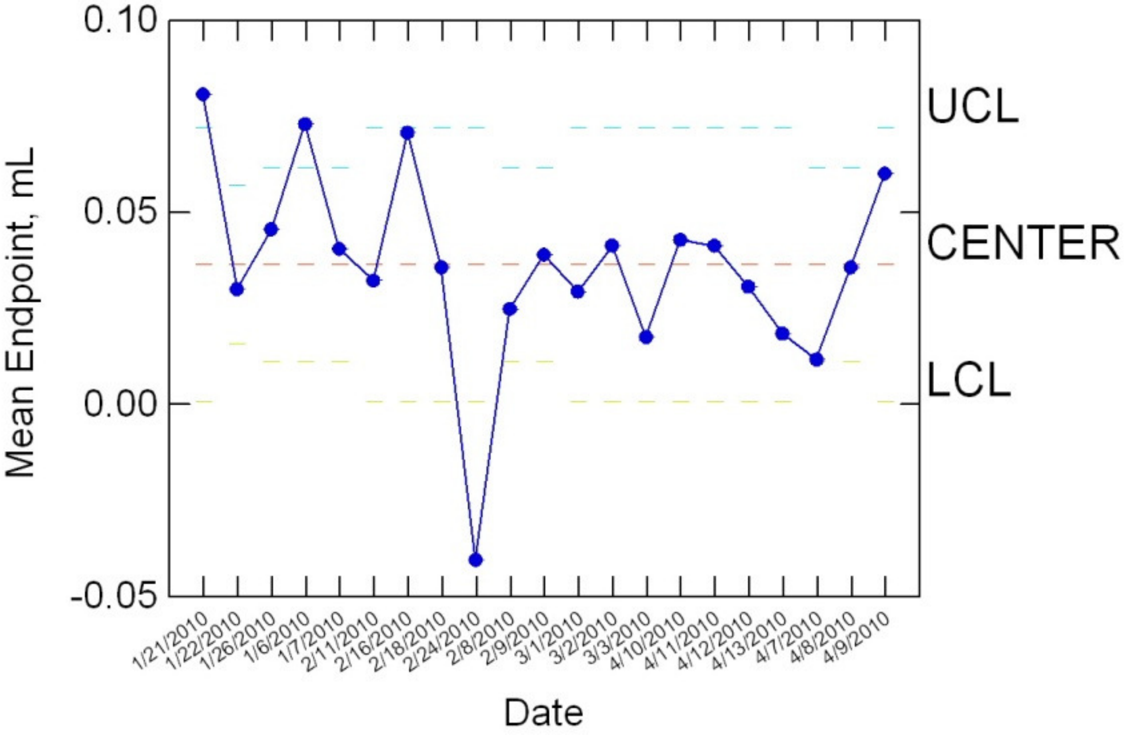

Figure 8-1. Shewhart chart of chloride end points (mL) obtained from Gran titrations of deionized water with 0.01 N silver nitrate and potentiometric measurements made with a silver/sulfide electrode.

It is recommended that a Shewhart chart or similar tool be used in FM 5-516 software to trend QA/QC measurements such as titration end points or chloride content in blank, chloride calibration, and laboratory control samples and to provide an indication when the method is out of control. The minimum sequence of 20 samples is recommended (Ellison et al., 2009) and chart "window" can move such that only the most recent samples are included in the chart.

9 Improvements to the Method

Improvements to the method fall into one of three categories: one, reducing ambiguity in the method; two, adding QA/QC steps to the method; and three, addressing the issue with low pH measurements.

9.1 Reducing Ambiguity

Performance of FM 5-516 differed to some extent between commercial laboratories and FDOT's Corrosion Laboratory: broadly, in terms of organization, cleanliness, and safety within the laboratory; specifically, in terms of interpreting particular steps of FM 5-516. For example, one commercial laboratory did not heat the rinse water and used 60 mL rather than 30 mL for rinsing; another laboratory weighed samples directly into a beaker rather than onto a pre-weighed watch glass. Results of a recent factor experiment (see Section 6-3) suggest that rinse water temperature may not have a significant effect on measured chloride concentration. A taring mistake, however, is a likely outcome when using a beaker instead of a pre-weighed watch glass for weighing the sample. It is recommended that FM 5-516 give explicit instructions for weighing the pulverized sample on a pre-weighed watch glass.

Another ambiguity between laboratories is the required number of blanks per sample, where a sample is analyzed in triplicate. It is recommended that FM 5-516 state that at a minimum one blank should be run for every 24 analyses (8 samples).

Accurate results of a Gran titration depend on accurate titrant delivery: titrant concentration and volume (see Sections 5, 6-5, 7-2). It is recommended that 0.0100 N titrant be prepared fresh each week, as over time evaporation of water from the titrant increases its strength and leads to an underestimate in chloride content. A specification for the accuracy of titrant delivery either in terms of equipment performance in combination with a technique for checking the accuracy is also recommended.

Other proposed changes to reduce ambiguity include:

- Specifying an ASTM method for sub-sampling crushed concrete prior to pulverization;
- Providing minimum electrode maintenance intervals;
- Defining the scaling potential; and
- Adding general guidance on process waste disposal.

9.2 Adding QA/QC Steps

In Table 3-1 are listed QA/QC activities that are appropriate for FM 5-516. Some of these activities such as matrix spikes and analysis of standard reference materials should be part of a laboratory's general practice rather than specific steps in a method. Some of the listed QA/QC activities, however, are recommended for inclusion in FM 5-516: a daily check of the electrode slope and analysis of trending of routine blank, 3 ppm chloride check standards (CCS), and laboratory control standards (LCS) prepared at chloride content near the level of detection (LOD). Trending of QA/QC samples to establish and maintain control limits is also recommended.

9.3 Low pH Extracts

Sample extract pH is not measured as part of FM 5-516, but as seen in Section 5 low pH can amplify systematic error inherent in titrant concentration or delivery volume. Ways to raise sample extract pH include:

- Use more sample
- Reduce nitric acid normality
- Reduce nitric acid volume
- Use a weaker acid (acetic acid, for example)
- Add a weak base such as sodium carbonate
- Add pulverized cement

Only the last two of the above-listed choices will raise the pH in a sand or rock that has little or no alkalinity. Kessler et al. (1978) appear to have the solved the problem of extract pH, for example, by measuring the chloride content of mixtures of sand, rock, and cement, rather than the separate components. One approach is to use 2.000 g of sample for cement to bring the sample extracts below pH 8; 4.000 g of sample for concrete to bring sample extracts up to pH 2, and 3.000 g of sand or rock plus 1.000 g of low-chloride cement for sand and rock that have little or no alkalinity. In this case, the laboratory could have on hand low-chloride cement that doubles as a laboratory control sample and as such is well-characterized. Presence of alkalinity as carbonate in sand and rock is easy enough to test with a drop of acid.

Reducing the scaling potential mitigates the low pH problem in sample extracts because a lower total titrant volume in needed to complete the titration; however, the silver/sulfide electrode does not seem stabilize as quickly at a lower scaling potential when the sample extract is below pH 2.

Refer to Appendix C for proposed changes to FM 5-516.

10 Planning an Inter-Laboratory Study

10.1 Study Elements

The proposed inter-laboratory study intends to characterize the chloride content of a reference material according to FM 5-516 to assess the method's precision and bias. For such a study, the reference material is a concrete batch.

Significant changes to FM 5-516 are proposed (Appendix C) and as such an inter-laboratory (also termed collaborative) study is recommended for the revised method. The term "round robin" is used to signify a repeated test of the same materials across several laboratories, that is, one inter-laboratory study may include several round robins.

Prior to conducting an inter-laboratory study, the revised method should be "tried, proved, and reduced to unequivocal written form" (ASTM D2777, 2008), for example, with a ruggedness study. A ruggedness study can be done by a single laboratory; however, ASTM C1067 (2007) recommends involvement of at least three laboratories.

ASTM C802 (2009) recommends that at least 10 laboratories participate in the inter-laboratory study. Likewise, ASTM D2777 (2008) requires that usable data must be acquired from at least six and preferably eight independent laboratories, which means "10 or more participating independent laboratories, as some laboratories will fail to provide usable data." If 10 laboratories cannot be found, ASTM C802 (2009) allows for a smaller group to repeat the program with the same samples six months apart.

The inter-laboratory study is proposed for one matrix—hardened concrete—at five nominal chloride concentrations: 0.10, 0.25, 0.40, 0.70, and 2.5 lbs/yd^3, to represent the LOD, LOQ, maximum allowable chloride concentrations (Table 1-1), and upper bound of the range over which FM 5-516 is considered valid (Appendix D).

Each concrete cylinder represents one sample. Concrete cylinders will be tested at each concentration in four round-robins, each ~2 weeks apart. The revised FM5-516 will be conducted for each sample, which means that three replicates of pulverized concrete from one cylinder will be analyzed and the average provided as one test result. Thus, four test results will be produced at each nominal chloride concentration. The two-week separation between round-robins is suggested to (1) allow laboratories to maintain a production schedule and (2) to review the interim data for incipient problems.

Each participating laboratory gets a copy of the revised FM 5-516, collaborative study instructions, data-reporting package, and samples; and instructions that include preliminary work required of participants to familiarize (or qualify) them with the method in advance of the study. Calibration materials and method reagents are not provided to study participants.

Samples are numbered in such a way as to not suggest or disclose the chloride concentrations. Assignment of samples to laboratories is randomized within concentrations levels; and the random order in which the samples are to be analyzed by the laboratories is also assigned (Section 10.2).

Prior to the official start date of the study, questions regarding the method, instructions, data sheets, or samples are solicited from the participants and a response to questions provided to all participants, with enough time allotted for this process to be repeated until there are no further questions.

Data should be handled and reported without censorship and with all figures obtained in the measurements and computer software reports, that is, no data rounding or truncation. Measurements that are below a laboratory's limit of quantitation (LOQ) or limit of detection (LOD) should be flagged as such.

10.2 Sampling Scheme

Ideally, a concrete batch at each of five nominal chloride concentrations is prepared in sufficient quantity that the entire batch is used for study samples. Forty 3-in x 6-in cylinders of hardened concrete are needed for each nominal chloride concentration.

Randomizing the laboratory assignment of each cylinder within a batch will reduce systematic (between-laboratory) error. In concrete cylinders poured from a concrete batch, chloride content likely varies because the distribution of aggregates and water in cylinders is different than that of the batch. For example, if the first cylinders poured from a batch have more water than the last cylinders, a chloride content gradient appears across the temporal sequence of sample collection. If laboratory 1 gets the first four cylinders and laboratory 10 gets the last four cylinders, a systematic error in reported chloride content emerges between laboratories.

If concrete batch is too large to be used in its entirety, the cylinders poured from the batch must be collected at random or alternately, the time that the first cylinder is poured from the batch is randomized, and the remaining 39 cylinders are poured at a fixed time intervals appropriate for the pour (ASTM E105, 2004).

Sample identification should not provide the destination laboratory with clues regarding chloride content. Table 10-1 is an example of randomized laboratory assignment and identification numbers for a sequence of cylinders from a batch pour; similar randomized cylinder assignments are made for each concrete batch.

Table 10-1 Example of Randomized Assignments for Samples from One Batch

	Laboratory									
Round Robin	1	2	3	4	5	6	7	8	9	10
1	ILS293	ILS308	ILS314	ILS281	ILS290	ILS298	ILS287	ILS294	ILS296	ILS289
2	ILS288	ILS313	ILS302	ILS291	ILS297	ILS286	ILS317	ILS301	ILS309	ILS279
3	ILS303	ILS307	ILS283	ILS282	ILS312	ILS311	ILS315	ILS300	ILS299	ILS304
4	ILS310	ILS284	ILS306	ILS305	ILS316	ILS285	ILS292	ILS295	ILS278	ILS280

Randomizing the analysis sequence of each study cylinder will also reduce systematic error within a laboratory. For example, if chloride concentrations are analyzed in order of increasing chloride and laboratory temperatures are cooler in the morning than in the afternoon, the results may biased relative to a laboratory whose temperature remains constant all day. To overcome this bias, low chloride concentrations should be analyzed both morning and afternoon; likewise high chloride concentrations should be analyzed both morning and afternoon. Table 10-2 is an example of randomized analysis sequence within a laboratory. Such a table is provided for each laboratory with sample instructions.

Table 10-2 Example of Randomized Analysis Sequence within a Laboratory

Round 1	Sample	A	C	B	D	E
	Sample ID	ILS293	ILS469	ILS226	ILS743	ILS710
Round 2	Sample	E	A	B	C	D
	Sample ID	ILS702	ILS288	ILS240	ILS476	ILS757
Round 3	Sample	E	C	B	D	A
	Sample ID	ILS688	ILS502	ILS223	ILS752	ILS303
Round 4	Sample	B	C	D	E	A
	Sample ID	ILS246	ILS486	ILS753	ILS685	ILS310

10.3 Data Analysis

Steps in data analysis include (ASTM D2777, 2008):

- Tabulating the data;
- Identifying and eliminating unusable data;
- Calculating precision and bias;
- Tabulating the statistics;
- Assembling the research report; and
- Preparing the precision and bias statement.

The first four steps in the data analysis are iterative; that is, each time a data point(s) is eliminated, the statistical analysis is repeated until no further data outliers are identified.

An initial review of the data should identify, if present, gross differences between individual and group measurements. An explanation should be sought from laboratories that produced errant data: first, in the event that a simple data entry error was made and can be corrected; and second, to understand better the possible source of error to justify its retention in or removal from the study database (ASTM D2777, 2008; ASTM C802, 2009). Beyond the more obvious data aberrations, both Youden (1975) and Steiner (1975), who are referenced in ASTM D2777 (2008), and ASTM E178 (2008) discuss ways to identify outlying laboratories and outlying individual results in collaborative study data.

Ellison et al. (2009) summarized widely used guidelines for outlier testing that will serve to update Youden (1975) and Steiner (1975), as necessary:

- Test at the 95% and 99% confidence level;
- All outliers should be investigated and corrected;
- Outliers at the 99% confidence level may be rejected unless there is a technical reason to retain them;
- Outliers significant only at the 95% confidence level should be rejected only if there is a technical reason to do so;
- Successive testing and rejection is permissible, but not to the extent of rejecting a large proportion of the data.

Testing at the 99% rather than the 95% confidence level is also recommended by ASTM E178 (2008).

10.4 Re-Analysis of FDOT Inter-Laboratory Study Data

Re-analysis of data from a previous FDOT inter-laboratory study of FM 5-516 (Kessler et al., 1982) afforded an opportunity for a step-wise data analysis. In this 1981 study, five laboratories were given two samples designated as 1-B and 2-A with chloride contents of 0.18 lbs/yd^3 and 0.40 lbs/yd^3, respectively. Samples were sent to the laboratories on two dates with a six-month interval between each date, under the assumption that six months was sufficient time for repeated measures to be considered independent. Samples were run in triplicate as required by the method and chloride concentrations were reported in units of lbs/yd^3. For contrast with the original work, this data re-analysis treated each triplicate dataset as one test result, with two test results produced by each of five laboratories. Note that for five laboratories, ASTM C802 (2009) recommends seven test results per laboratory. Refer to Table 10-3 for a data summary.

Table 10-3 Re-Analysis Tabulated Data (units are lbs chloride/yd^3 concrete)

Laboratory	Sample 1-B				Sample 2-A			
	Round 1	Round 2	Average	Variance	Round 1	Round 2	Average	Variance
1	0.241	0.214	0.228	0.000374	0.468	0.470	0.469	0.000004
2	0.139	0.203	0.171	0.002069	0.400	0.384	0.392	0.000128
3	0.191	0.224	0.207	0.000544	0.421	0.403	0.412	0.000150
4	0.178	0.195	0.187	0.000156	0.381	0.431	0.406	0.001284
5	0.203	0.179	0.191	0.000280	0.416	0.307	0.361	0.005977

A Kolmogorov-Smirnov (K-S) test was first applied to check that sample data were normally distributed (Ellison et al., 2009). Dixon's Q test (ASTM E178, 2008) was used to screen for high and low outliers in the datasets and was not significant for either sample at the 95% confidence level. The variance for laboratory 5 is high compared to variances seen in laboratories 1 through 4 for sample 2-A based on an F-test; thus, data from laboratory 5 and sample 2-A are candidate for removal but were not removed for this analysis.

A one-factor analysis of variance (ANOVA; Microsoft Excel 2007) was performed to test the hypothesis that sample means from each laboratory were the same and to estimate the repeatability and reproducibility standard deviations and precision limits for FM 5-516. Refer to Tables 10-4 and 10-5 for ANOVA results for each sample.

Table 10-4 ANOVA Results for Sample 1-B

Source of Variation	SS	df	MS	F	P-value	F crit
Between Labs	0.003744	4	0.000936	1.367162	0.363538	5.192168
Within Labs	0.003424	5	0.000685			
Total	0.007168	9				

Table 10-5 ANOVA Results for Sample 2-A

Source of Variation	SS	df	MS	F	P-value	F crit
Between Labs	0.01235	4	0.003087	2.04673	0.225924	5.192168
Within Labs	0.007542	5	0.001508			
Total	0.019892	9				

ANOVA for both samples indicated no significantly different mean chloride concentrations were found between laboratories when tested at the 95% confidence level ($p < 0.05$). Estimates of within-laboratory variance s_w^2 and between-laboratory variance s_b^2 were computed from ANOVA results according to Equations 10-1 and 10-2, respectively, where M_w is the within-lab mean-squared error and M_b is the between-lab mean-squared error, and N is the number of replicates. Variances that correspond to single-level precision (within laboratories or repeatability, s_r) and multi-laboratory precision (between laboratories or reproducibility, s_R) were estimated from Equations 10-1 and 10-3, respectively, and are shown in Table 10-6. Note that with triplicate measurements of the same sample treated as one test result, the within-laboratory component of the variance is now greater than the between-laboratory component (Table 10-6).

$$s_w^2 = M_w = s_r^2 \tag{10-1}$$

$$s_b^2 = \frac{M_b - M_w}{N} \tag{10-2}$$

$$s_R^2 = s_w^2 + s_b^2 \tag{10-3}$$

Table 10-6 Averages, Components of Variances, and Variances

Sample	Averages	Components of Variance		Variances	
		Within Labs	Between Labs	Within Labs	Between Labs
1-B	0.197	0.000685	0.000126	0.000685	0.000810
2-A	0.408	0.001508	0.000789	0.001508	0.002298

Standard deviations that correspond to single-level precision (within-laboratory or repeatability, s_r) and multi-laboratory precision (between-laboratory or reproducibility, s_R) are shown in Table 10-7. Note that as chloride content increased, standard deviations increased but coefficients of variation (CV) decreased, as was seen by Kessler et al. (1982).

Table 10-7 Averages, Standard Deviations, and Coefficients of Variation

Sample	Averages	Standard Deviations		Coefficients of Variation	
		Within Labs	Between Labs	Within Labs	Between Labs
1-B	0.197	0.0262	0.0285	13.3	14.5
2-A	0.408	0.0388	0.0479	9.5	11.7

10.5 Precision and Bias Statements

The following are examples of precision statements drawn from the re-analyzed data for sample 2-A:

> Data used to develop this precision statement were obtained using an earlier vesion of FM 5-516. The single-operator coefficient of variation has been found to be 10%. Therefore, results of two properly conducted tests by the same operator on the same material are not expected to differ by more than 28% of their average. Note that triplicate subsamples from one sample analyzed in accordance with FM 5-516 represents one test result. These numbers represent the (1s) and (d2s) limits as described in ASTM Practice C670 Preparing Precision Statements for Construction Materials.

> Data used to develop this precision statement were obtained using an earlier vesion of FM 5-516. The multi-laboratory coefficient of variation has been found to be 12%. Therefore, results of two different laboratories on identical samples of a material are not expected to differ from each other by more than 34% of their average. Note that triplicate subsamples from one sample analyzed in accordance with FM 5-516 represents one test result. These numbers represent the (1s) and (d2s) limits as described in ASTM Practice C670 Preparing Precision Statements for Construction Materials.

Bias is determined from the difference between a reference value and experimental value, as shown in Equation 10-4 (Youden, 1975; Skoog et al., 1996), where t is calculated for either a one-sided or a two-sided Student's t test, as appropriate, at the 95% or 99% confidence level for N-1 degrees of freedom, $\bar{x}_2$ is the mean of experimental values, μ the mean of the reference value, s is the standard deviation of experimental values, and is the number of difference pairs. The difference between the experimental mean and the reference mean was within the 95% confidence interval for both sample 1-B and 2-A; thus, estimated biases were not significant.

$$\bar{x} - \mu = \frac{ts}{\sqrt{N}} \qquad (10\text{-}4)$$

In this case, an example bias statement is (ASTM C670, 2003):

> When experimental results are compared with known values from accurately compounded specimens, the test method is found to have no bias.

10.6 <u>How Many Replicates?</u>

An inter-laboratory study can answer several questions relevant to method performance:

(1) For a given batch of concrete, is the variance between samples (cylinders) the same as the variance within samples (cylinders)?
(2) What is the relationship between reproducibility s_R and chloride content in concrete?
(3) How many replicates are needed?

The following is an example approach for estimating the number of replicates from a concrete cylinder if the within-cylinder variance is equal to or greater than between-cylinder variance for a given concrete batch, or in other words, if one concrete cylinder is representative of the entire batch. For this example, due to limited information on method reproducibilty s_R, method repeatability s_r (Equation 6-8) was used.

The maximum allowable chloride content is established such that if the test result from a properly executed FM 5-516 exceeds 0.40 lbs/yd^3, then the chloride content is unambiguously greater that the target chloride content of 0.30 lbs/yd^3 (Kessler et al., 1982) and the concrete must be rejected.

Figure 10-1 shows the relationship between the probability that the chloride concentration is not different from 0.30 lbs/yd^3 and average chloride concentration assuming that standard deviation s_r is a function of chloride concentration (Equation 6-8) and for an average concentration that was based on either duplicate (N = 2) or triplicate (N = 3) measurements of the sample.

For triplicate measurements, there was a 5% chance that a chloride concentration of 0.36 lbs/yd^3 was equal to 0.30 lbs/yd^3; or in other words, at the 95% confidence level, a chloride concentration greater than 0.36 lbs/yd^3 exceeded the target chloride content. For duplicate measurements, at the 95% confidence level, a chloride concentration greater than 0.55 lbs/yd^3 exceeded the target chloride content. Thus, FM 5-516 should require at least triplicate measurements of the sample.

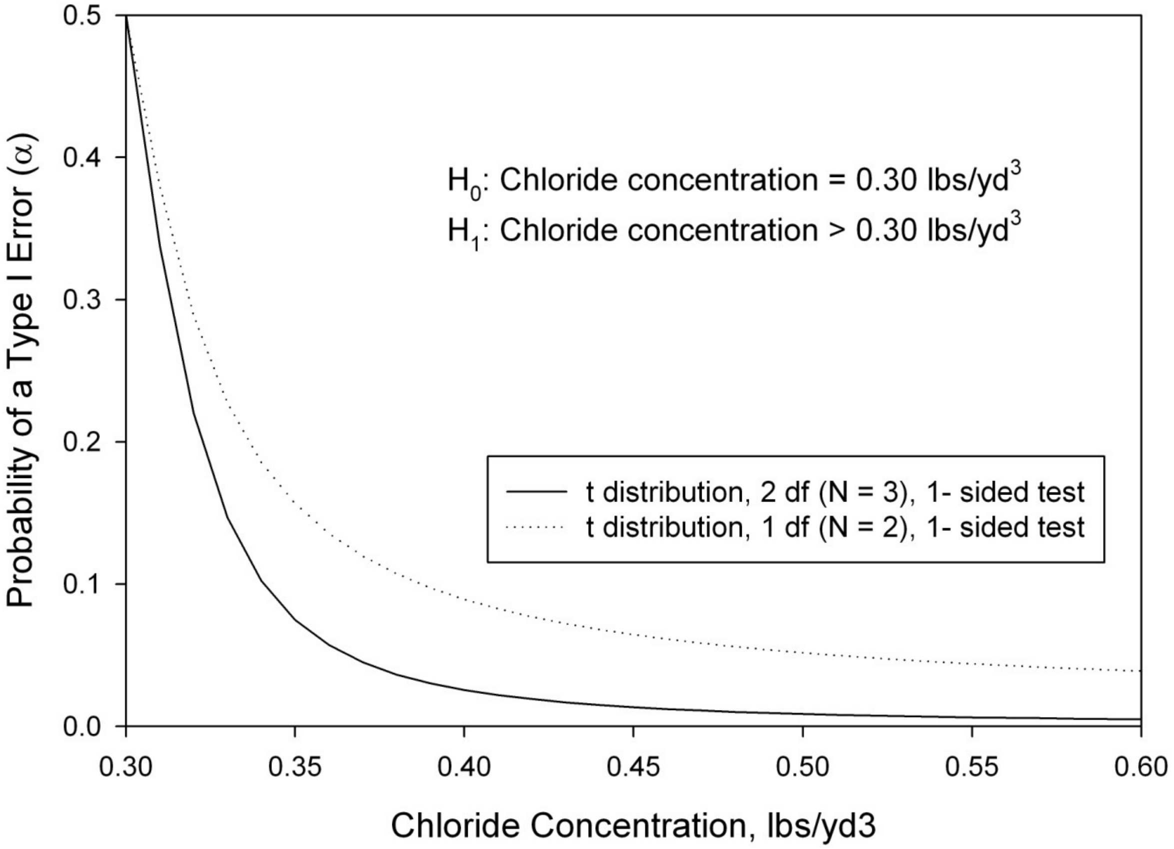

Figure 10-1. Probability of a type I error (α) versus chloride concentration in concrete for chloride concentrations between 0.30 and 0.60 lbs/yd^3.

10.7 Qualifying a Laboratory for the Revised FM 5-516

Inherent in the revised FM 5-516 are control limits for QA/QC samples including blanks, 3 ppm chloride check standards (CCS) and laboratory control standards (LCS). At least 20 replicates of each QA/QC standard are needed to establish the control limits; thus, to qualify for this method a laboratory must as a minimum analyze the following samples:

- 20 blanks;
- 20 CCS from a reputable source;
- 20 concrete LCS;
- 20 cement LCS; and
- One independent or standard reference material with chloride content within the method range.

The average chloride end point measured in the blanks must be within -0.1 and +0.1 mL when titrated with 0.0100 N and 0.100 N $AgNO_3$.

Chloride check standards (CCS) must be within 5% of their target concentration of 3.00 ppm.

The range of three replicates of the concrete and cement laboratory control samples (LCS) must be equal to or less than 0.080 lbs/yd^3.

Test results must be "in control" according to Chloride 2010 software.

The average chloride concentration found by FM 5-516 for an independent reference material (IRM) must not be significantly different at the 95% confidence level from the IRM-certified concentration, based on a two-tailed Student's t-test for accuracy and an F-test for precision.

10.8 Results Summary

Development of precision and bias statements for the revised FM 5-516 has two stages: first, a ruggedness study to be accomplished in accordance with ASTM C1067 (2007), and second, an inter-laboratory study to be done in accordance with ASTM 802 (2009). The product of the first stage is a method that is in its final form for the inter-laboratory study. Proposed for the second stage is a 10-laboratory study where samples at five target levels of chloride: 0.10, 0.25, 0.40, 0.70, and 2.5 lbs/yd^3 are presented to the laboratories as cylinders in four round-robins, where each round-robin is separated by two weeks. In this study, performance of FM 5-516 will yield one test result. Laboratories recruited for this effort will need to qualify on the revised FM 5-516 prior to the start of the study.

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Appendix A Comparison of Ion-Selective Electrode Methods for Chloride Determination

Table A-1 Comparison of Ion-Selective Electrode Methods for Chloride Determination

Feature	FM 5-516 (2005)	AASHTO T260 (2001)	ASTM D512 (2004)
Range of chloride concentration	Up to 625 ppm (2.5 lb/yd^3)	Not addressed	2-1,000 mg/L
Electrode	Required: Orion 96-17 combination chloride electrode or Orion 94-16 silver/sulfide electrode with an Orion 90-02 double junction reference electrode	Suggested: Orion 96-17 combination chloride electrode or Orion 90-02 silver/sulfide electrode	Chloride ion-selective electrode in conjunction with a double junction, sleeve-type reference electrode; silver chloride/silver sulfide membranes are not appropriate
Millivolt meter	pH/mV meter with a 0.1 mV resolution	Suggested: Orion Model 701 A digital pH/mV meter or equivalent	pH/mV meter
Burette	Not applicable	0.1-mL graduations	Not applicable
Pipettor	0.5 mL fixed volume dispensing capacity and an opaque brown glass reservoir bottle	Not applicable	Not applicable
Balance	Analytical balance capable of weighing a sample with a precision of 1 mg	Compliance with M 231, Class A	Not addressed
Balance	---	Compliance with M 231, Class G2	Not applicable
Hot plate	250° C heating surface temperature	250° -400° C heating surface temperature	Not applicable
Sieve	US Standard, 300 µm (No. 50)	US Standard, 300 µm (No. 50)	Not applicable
Filters	Whatman No. 41 filter papers, chloride-free	Whatman No. 40 and No. 41 filter papers, chloride-free	Not applicable
Nitric acid	1:12 nitric acid solution	Concentrated, specific gravity 1.42	Concentrated, specific gravity 1.42, containing less than 0.005% chloride
Sodium chloride	Not addressed	Reagent grade (primary standard); prepared to 0.01 N	Reagent grade, prepared as a stock solution of 1,000 mg/L and for standards of 100, 10, and 1 mg/L
Silver nitrate	Reagent grade prepared to 0.1 N and 0.01 N, stored in brown glass bottle	Reagent grade (standardized to NaCl) prepared to 0.01 N	Not applicable
Water	De-ionized	Distilled or de-ionized	Type I reagent water conforming to D1193
Indicator	Not addressed	Methyl orange	Not applicable
Feature	FM 5-516 (2005)	AASHTO T260 (2001)	ASTM D512 (2004)

Feature	FM 5-516 (2005)	AASHTO T260 (2001)	ASTM D512 (2004)
Hydrogen peroxide	Not addressed	30%	Not addressed
Ionic strength adjustor	Reagent grade potassium nitrate, 15 g/100 ml de-ionized water	Not addressed	Reagent grade sodium bromate, containing less than 0.003% chloride; 15.1 g/800 ml water to which is added 75 ml nitric acid
Concrete pulverization	Crushing and pulverizing apparatus; crush sample such that largest particles are less than 1.3 cm diameter and sample weight is ~400 g; dry sample in oven at 110°C for 2-4 hours, then pulverize to pass through a No. 50 sieve	Rotary impact-type drill; crush or grind dry concrete to pass through a No. 50 sieve; clean tools with alcohol and dry before use with separate samples. (Drying in oven at 105°C is optional)	Not applicable
Depth determination for drilling to concrete	Not addressed	Pachometer capable of determining location and depth of reinforcing steel to ± 3 mm (0.125 in.)	Not applicable
Mass of concrete powder	3.000 g	3.000 g	Not applicable
Method	Acid-soluble chloride; Gran plot	Acid-soluble or water-soluble chloride; Potentiometric titration or Gran plot	Chloride in water; potentiometric
End point for Gran plot method	Determined by software	225 ± 5 mV (chloride electrode) or 310 ± 5 mV (silver/sulfide electrode)	Not applicable
Software	Chloride 2000	Not applicable	Not applicable
QA/QC	Analyze three replicates of each sample; analyze a reagent water test blank with each sample	Not addressed	Analyze 7 replicates of an independent reference material containing a mid-range concentration of chloride; analyze a laboratory control sample after every 10 samples; analyze a reagent water test blank with each batch of samples; check for interferences using a matrix spike; analyze a duplicate sample in each batch

Appendix B Glossary of Selected Quality Assurance/Quality Control (QA/QC) Terms

accuracy—measure of the degree of conformity of a single test result generated by a specific procedure to the assumed or accepted true value, and includes both precision and bias (ASTM D2777, 2008).

batch—set (group) of samples analyzed such that results of analysis of the QC samples (laboratory control sample, method blank, matrix spike, and duplicate or matrix spike duplicate) analyzed with the batch are indicative of the quality of the results of analysis of samples in the batch. When results from tests of any of the QC samples associated with the batch fail to meet the performance criteria, the test method should define the appropriate corrective action. To make such a response valid, the batch shall be constructed in such a way as to assure that all variables affecting the batch will affect all samples in the batch in a statistically equivalent manner (ASTM D1129, 2010).

bias—the persistent positive or negative deviation of the average value of a test method from the assumed or accepted true value (ASTM D2777, 2008).

calibration curve—plot of the potential (emf) of a given ion-selective electrode cell assembly (ion-selective electrode combined with an identified reference electrode) versus the logarithm of the ionic activity (concentration) of a given species. For uniformity, it is recommended that the potential be plotted on the ordinate (vertical axis) with the more positive potentials at the top of the graph and that p*aA* (-log activity of the species measured, *A*) or p*cA* (-log concentration of species measured, *A*) be plotted on the abscissa (horizontal axis) with increasing activity to the right (ASTM D4127, 2006).

calibration standard—solution containing the analyte of interest at a known concentration either purchased from an external source or prepared in-house from materials of known purity or concentration, or both, and used to calibrate the measurement system (ASTM D1129, 2010).

independent reference material (IRM)—(may be interchanged with **standard reference material** or **certified reference material**) material of known purity and concentration obtained either from the National Institute of Standards and Technology (NIST) or other reputable supplier. The IRM shall be obtained from a different lot of material than is used for calibration (ASTM D1129, 2010).

instrumental detection limit (IDL)—concentration equivalent to a signal, which is equal to three times the standard deviation of the blank signal at the selected analytical mass(es) (ASTM D1129, 2010).

interfering substance—any species, other than the ion being measured, whose presence in the sample solution affects the measured potential of a cell. Interfering substances fall into two classes: "electrode" interferences and "method" interferences. Examples of the first class would be those substances which give a similar response to the ion being measured and whose presence generally results in an apparent increase in the activity (or concentration) of the ion to be determined (for example, Na+ for the Ca++ electrode), those species which interact with the membrane so as to change its chemical composition (that is, organic solvents for the liquid or poly(vinyl chloride) (PVC) membrane electrodes) or electrolytes present at a high concentration giving rise to appreciable liquid-junction potentials. The second class of interfering substance is that which interacts with the ion being measured so as to decrease its activity or apparent concentration, but where the electrode continues to report the true activity (that is, CN- present in the measurement of Ag+) (ASTM D4127, 2006).

laboratory—a single and completely independent analytical system with its own specific apparatus, source of reagents, set of internal standard operating procedures, etc. Different laboratories will differ from each other in all of these aspects, regardless of how physically or organizationally close they may be to each other (ASTM D2777, 2008).

laboratory control sample (LCS)—sample of known concentration and composition that is taken through the entire test method to determine whether the analytical system is in control. The LCS must be prepared in the appropriate ASTM-grade water from a material that sufficiently challenges the test. The LCS can be an IRM obtained from an outside source or prepared in-house from materials of known purity and concentration. Alternatively, the LCS may be a real sample of the matrix that is typically analyzed and which has been fully characterized (ASTM D1129, 2010).

matrix spike—quantity (mass) of a component (analyte) of interest which is added to a sample (matrix) in order to test bias as measured by recovery (of that component under specific analytical conditions) and reported as percent recovery (*P*) (ASTM D1129, 2010).

method blank (MB)—suitable aliquots of reagent water are analyzed using the same sample preparation technique, analytical method and QA/QC procedure used for test samples. The MB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents or apparatus (ASTM D1129, 2010).

multi-laboratory precision—(often interchanged with **between-laboratory error** and **systematic error**) provides an estimate of the difference that may be expected between measurements made on the same material in two different laboratories (ASTM C802, 2009). See also **reproducibility**.

operator—usually the individual analyst within each laboratory who performs the test method throughout the collaborative study. However, for complicated test methods, the operator may be a team of individuals, each performing a specific function throughout the study (ASTM D2777, 2008).

precision—degree of agreement of repeated measurements of the same property, expressed in terms of dispersion of test results about the arithmetical-mean result obtained by repetitive testing of a homogeneous sample under specified conditions. The precision of a test method is expressed quantitatively as the standard deviation computed from the results of a series of controlled determinations (ASTM D2777, 2008).

range—the region defined by the minimum and maximum measurable limits (ASTM D1129, 2010)

relative standard deviation (RSD)—relative standard deviation of the mean expressed as a percentage (also known as coefficient of variation) (ASTM D1129, 2010).

repeatability—measure of the precision of one analyzer to repeat its results on independent introduction of the same sample at different time intervals. (ASTM D1129, 2010) See also **single-operator precision**.

reproducibility—measure of the precision of different analyzers to repeat results on the same sample (ASTM D1129, 2010). See also **multi-laboratory precision**.

single-operator precision—(often interchanged with **within-laboratory error** and **random error**) provides an estimate of the difference that may be expected between duplicate measurements made on the same material in the same laboratory by the same operator using the same apparatus within the time span of a few days (ASTM C802, 2009). See also **repeatability**.

standard solution, stock—a concentrated solution containing a single certified standard that is an analyte or a concentrated solution of a single analyte prepared in the laboratory with an assayed reference compound. Stock standard solutions are used to prepare secondary dilution standards (ASTM D1129, 2010).

Appendix C Revised Florida Method of Test FM 5-516

Proposed changes are highlighted in yellow.

Effective: September 1, 2000
Revised: December 14, 2010

Florida Method of Test
For
Determining Low-Levels of Chloride in Concrete and Raw Materials

Designation: FM 5-516

1. SCOPE

1.1 This method covers the determination of total chloride content in cement, fine aggregate, coarse aggregate, and concrete. The method is applicable to chloride contents lower than 100 parts per million (about 0.40 lb/yd^3), but will accurately measure contents as high as 625 ppm (about 2.5 lb/yd^3).

2. REFERENCED DOCUMENTS

2.1 ASTM Standards:

ASTM C 702 Standard Practice for Reducing Samples of Aggregate to Testing Size

3. PRECISION AND BIAS STATEMENTS

3.1 Precision:

Data used to develop this precision statement were obtained using an earlier vesion of FM 5-516. The multi-laboratory coefficient of variation has been found to be 12%. Therefore, results of two different laboratories on identical samples of a material are not expected to differ from each other by more than 34 % of their average. Note that triplicate subsamples from one sample analyzed in accordance with FM 5-516 represents one test result. These numbers represent the (1s) and (d2s) limits as described in ASTM Practice C670 Preparing Precision Statements for Construction Materials.

3.2 Bias:

When experimental results are compared with known values from accurately compounded specimens, the test method is found to have no bias.

4. APPARATUS

4.1 Crushing and pulverizing apparatus capable of grinding a sample to pass a 50 mesh sieve.

4.2 Analytical balance capable of weighing a sample with a precision of 1 mg.

4.3 Hot plate with a heating surface temperature of approximately 250 °C.

4.4 Glassware: 100-ml beakers, 250-ml beakers, 100-ml volumetric flasks, 1000-ml volumetric flask, 2,000-ml volumetric flask, watch glasses, filter funnels, 250-ml graduated cylinder, 10-ml graduated cylinder, 10-ml volumetric pipette, 3-ml volumetric pipette, and 1-ml pipette.

4.5 Filter paper: Whatman No. 41 or equivalent. Any equivalent paper should be checked for chloride content before using.

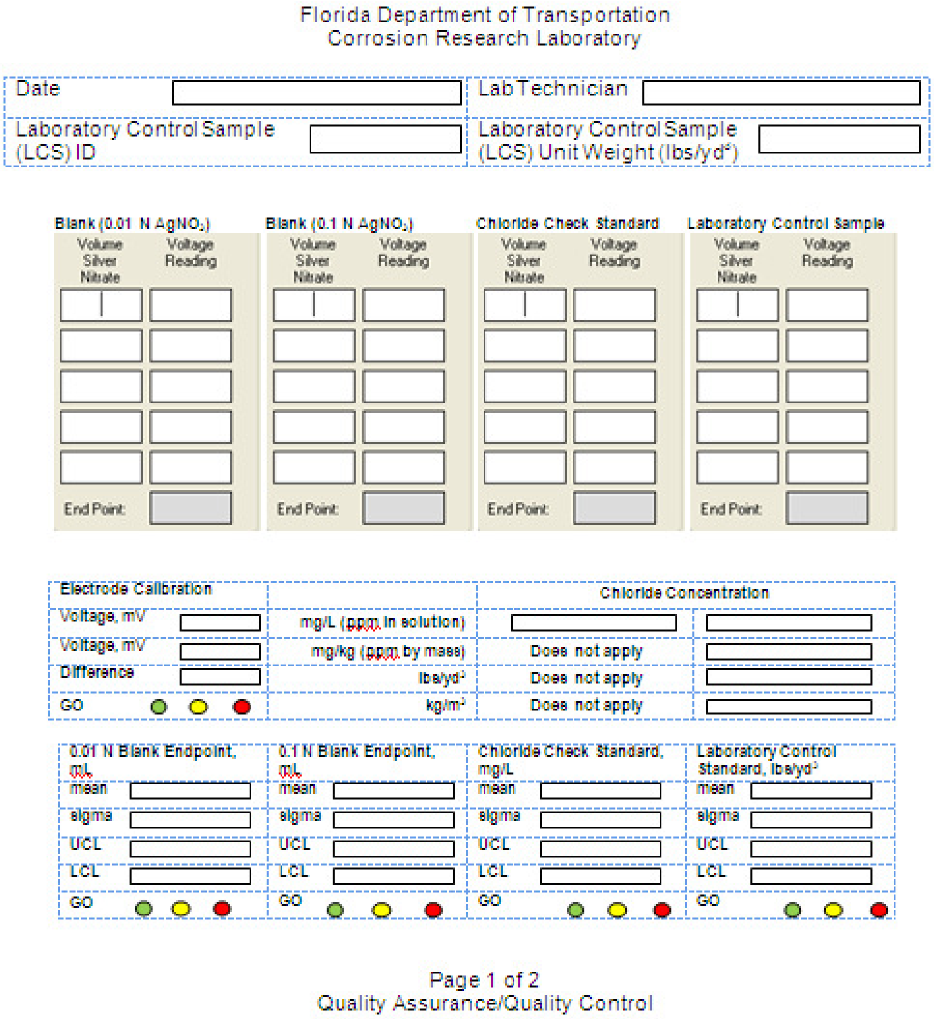
4.6 Magnetic stirrer and Teflon-coated stir bar.

4.7 Fixed volume dispenser with 0.5-ml dispensing capacity and a maximum error limit for a single measurement of 2% (0.01 mL) and an opaque brown glass reservoir bottle (two each), and fixed volume dispenser with 35.0 ± 0.1 ml dispensing capacity and a maximum error limit for a single measurement of 1% (0.35 mL) and an opaque brown glass reservoir bottle.

4.8 Chloride ion or silver/sulfide ion-selective electrode with manufacturer's recommended filling solutions replaced at the recommended intervals. Recommended are Orion 96-17 combination chloride electrode, Orion 96-16 combination silver/sulfide electrode, or Orion 94-16 silver/sulfide electrode with an Orion 90-02 double junction reference electrode.

4.9 pH/mV meter with a 0.1 mV resolution for use with electrodes in 4.8.

4.10 Software package “Chloride 2010” available for all FDOT approved chloride laboratories (Figure 1). Software calculates chloride content in weight %, ppm, lb/yd^3, kg/m^3 based on the measurements taken using this test method.



Florida Department of Transportation
Corrosion Research Laboratory

Date		Lab Technician	
Laboratory Control Sample (LCS) ID		Laboratory Control Sample (LCS) Unit Weight (lbs/yd^3)	

Blank (0.01 N $AgNO_3$)		Blank (0.1 N $AgNO_3$)		Chloride Check Standard		Laboratory Control Sample	
Volume Silver Nitrate	Voltage Reading	Volume Silver Nitrate	Voltage Reading	Volume Silver Nitrate	Voltage Reading	Volume Silver Nitrate	Voltage Reading
End Point:		End Point:		End Point:		End Point:	

Electrode Calibration			Chloride Concentration	
Voltage, mV		mg/L (ppm in solution)		
Voltage, mV		mg/kg (ppm by mass)	Does not apply	
Difference		lbs/yd^3	Does not apply	
GO	● ● ●	kg/m^3	Does not apply	

0.01 N Blank Endpoint, mL		0.1 N Blank Endpoint, mL		Chloride Check Standard, mg/L		Laboratory Control Standard, lbs/yd^3	
mean		mean		mean		mean	
sigma		sigma		sigma		sigma	
UCL		UCL		UCL		UCL	
LCL		LCL		LCL		LCL	
GO	● ● ●	GO	● ● ●	GO	● ● ●	GO	● ● ●

Page 1 of 2
Quality Assurance/Quality Control

Figure 1. Overview of Chloride Software input and output data fields.

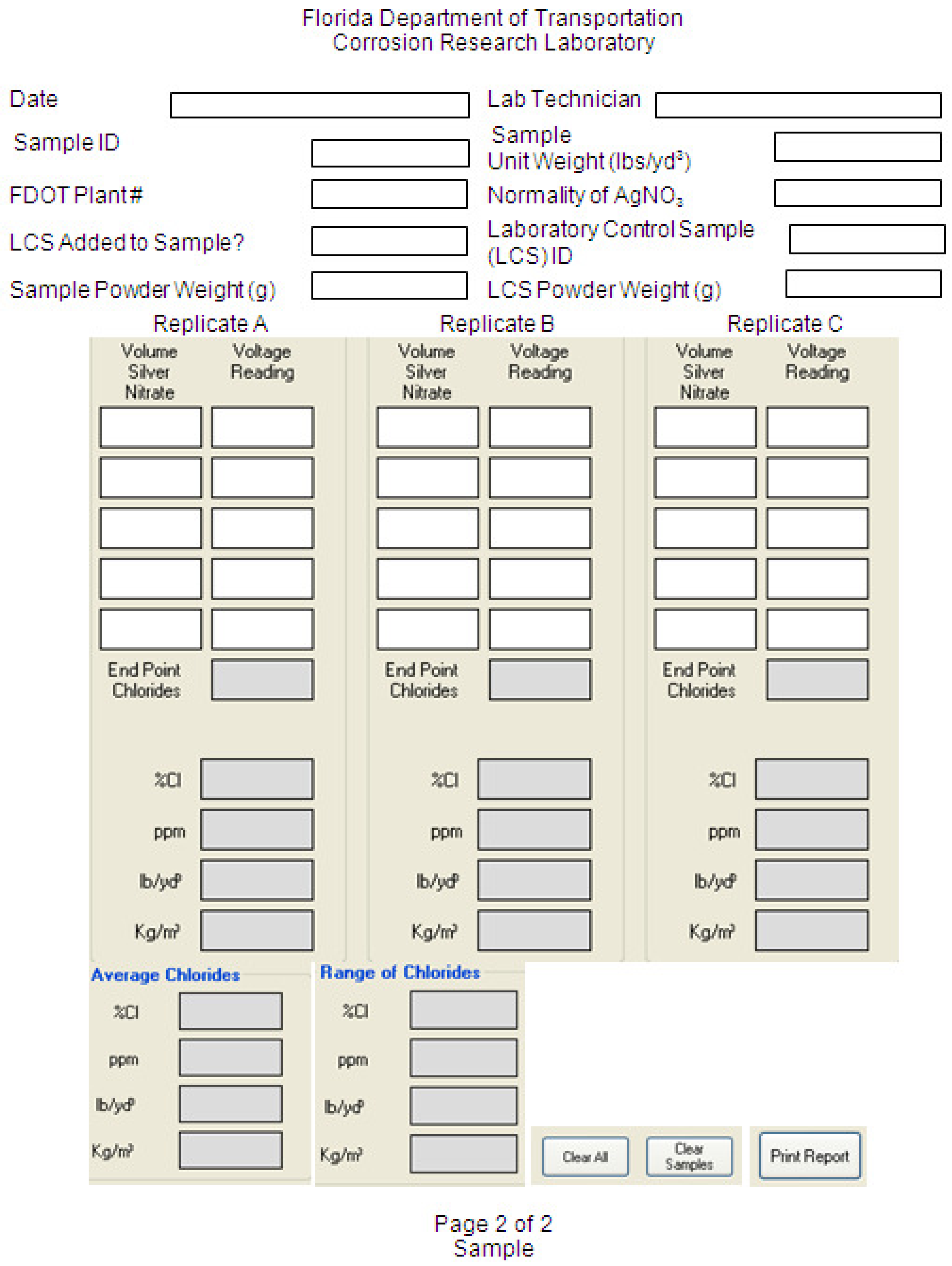


Figure 1. Overview of Chloride Software input and output data fields (continued).

5. REAGENTS

5.1 5% Nitric Acid Solution: Fill a 2-liter volumetric flask with 1800 ml of deionized water. Under a chemical fume hood, measure 150 ml of concentrated (~70%) HNO_3 acid into a 250-ml graduated cylinder. Slowly add the HNO_3 acid to the deionized water. DO NOT add the water to the acid. Still under the hood, rinse the graduated cylinder with ~50 mL of deionized water (the acid residue will fume) and add the rinsate to the volumetric flask to bring the total solution volume up to 2 liters.

5.2 0.1 N Silver Nitrate Solution: Weigh 16.987 g of reagent grade $AgNO_3$ and transfer to a 1000-ml volumetric flask. Add enough deionized water to the flask to dissolve the $AgNO_3$, then fill with deionized water and mix thoroughly. Alternately, obtain a 1-liter 0.100 N $AgNO_3$ standard solution from a reputable supplier. Store the solution in a cabinet in an opaque and chemically-resistant bottle away from any light source. Silver nitrate solutions will deteriorate when exposed to light, so a dark storage place is essential for stability. Evaporation of water from silver nitrate solution will tend to concentrate the silver nitrate over time.

5.3 0.01 N Silver Nitrate Solution: Prepare a 1:10 dilution of 0.1 N silver nitrate. Prepare fresh each week. Store the solution in a cabinet in an opaque and chemically-resistant bottle away from any light source. Silver nitrate solutions will deteriorate when exposed to light, so a dark storage place is essential for stability. Evaporation of water from silver nitrate solution will tend to concentrate the silver nitrate over time.

5.4 Low-Level Ionic Strength Adjuster (ISA) Solution: Weigh 15.0 g of reagent grade KNO_3 and dissolve it in 100 ml of deionized water. Store this solution in an opaque and chemically-resistant bottle.

5.5 1000 mg/L Chloride Standard Solution: Dry reagent grade NaCl for 2 hours in an oven at 105 ^{o}C. Cool in a dessicator, and once cooled weigh out 1.649 g, dissolve in deionized water, and transfer to a 1-liter volumetric flask. Make up to the mark with deionized water. Alternately, obtain a NIST-traceable 1000 mg/L chloride standard solution from a reputable supplier. Use this standard solution for the electrode calibration curve.

5.6 100 mg/L Chloride Standard Solutions: Obtain or prepare a NIST-traceable 100 mg/L chloride standard solution from a source different from that of the 1000 mg/L standard solution. Use this standard solution to prepare the 3-ppm chloride check standard.

6. SAMPLE PREPARATION

6.1 Hardened Concrete: A concrete field sample should be comparable to 15 cm X 30 cm (6 in X 12 in) or 10 cm X 20 cm (4 in X 8 in) or 7.6 cm X 15 cm (3 in X 6 in) standard cylinder molds. Crush the sample such that the largest particles are no larger than 1.3 cm (0.5 in) in diameter. Reduce the sample size down to approximately 400 g in accordance with ASTM C 702. Dry the sample in an oven at 110 ^{o}C (230 ^{o}F) for 2 to 4 hours. After sample has dried, pulverize the material until the entire sample will pass a 50 mesh sieve.

6.2 Aggregates: A coarse aggregate field sample should be one bag or approximately 16 kg (35 lb). A fine aggregate sample should be half a bag or approximately 14 kg (30 lb). Reduce the aggregate field sample to approximately 400 g. If the aggregate is larger than 1.3 cm (0.5 in) in diameter, first crush the sample. Dry the sample in an oven at 110 ^{o}C (230 ^{o}F) for 2 to 4 hours. After sample has dried, pulverize the material until the entire sample will pass a 50 mesh sieve.

6.3 Cement: The cement field sample should fill a half gallon can. Pass the sample through a 20 mesh sieve in order to mix the sample, break up lumps, and remove foreign materials.

6.4 Laboratory Control Sample (LCS): Prepare both a hardened concrete and cement LCS with chloride content near 0.1 lb/yd^3 as described in 6.1 and 6.3, respectively, in sufficient quantity for routine monitoring of method performance over the course of one or more years.

6.5 Storage: Store the powdered samples in chemically-inert covered containers that are clean and dry.

7. PROCEDURE

7.1 Total Chloride Extraction from Cementitious Materials: Prepare each of triplicate samples by weighing the mass of material required by Table 1 onto a pre-weighed watch glass. Transfer each sample replicate to a 100-ml beaker. Add 5 ml of deionized water to each beaker and swirl or stir to break up any clumps that may have formed. Slowly add 35 ml of the 5% nitric acid solution to each beaker (care should be exercised to avoid excessive frothing). Place the beakers on the hot plate and watch glasses on the beakers. Heat the samples over medium heat (approximately 250 ^{o}C) until they boil. Allow samples to boil gently for 2 to 4 minutes. Samples which contain blast furnace slag have significant levels of sulfides. Sulfide ions will interfere with the operation of the Orion 94-16 Silver/Sulfide electrode and may cause erroneously high chloride results. These samples will require additional boiling and possibly the addition of 4 or 5 drops of concentrated HNO_3 to drive the sulfide ions off as hydrogen sulfide. A secondary test is required to verify the absence of sulfide ions; Hach Company (www.hach.com) sells an easy to use sulfide test kit (HS-C 25378-00) for this purpose. Remove the samples from the hot plate and filter through a Whatman No. 41 filter paper into 100-ml volumetric flasks. Rinse the residue in the filter two or three times with approximately 30 ml of hot deionized water. Allow the samples to cool to room temperature (about 1 hour), then add deionized water to the mark on the flasks.

Table 1. Mass of Cementitious Material

Material	Mass, g
Cement	2.000
Concrete	4.000

7.2 Total Chloride Extraction from Aggregate Materials: Prior to weighing out samples, place a watch glass under the chemical hood and add ~ 0.5 g of sample followed by a few drops of 5% nitric acid. If aggregate fails to froth with the addition of acid, prepare triplicate samples by weighing 3.000 g of material with 1.000 g of cement LCS onto a pre-weighed watch glass; otherwise prepare each of triplicate samples by weighing 3.000 g of material onto a pre-weighed watch glass. Continue with the procedure in Section 7.1 as written.

7.3 Electrode Maintenance: Flush the filling solution from the electrode and refill the electrode with fresh solution at least once per day and after every 24 analyses (8 samples). Restore the electrode membrane as described in the manufacturer's electrode manual at least once per day or more often if the electrode response appears sluggish. Follow the manufacturer's guidance for conditioning the electrode after restoring the membrane, and for both short-term (<2 weeks) and long-term electrode storage.

7.4 Electrode Calibration Curve: At least once per day at the start of sample analyses, check that the slope of the calibration curve is within the manufacturer's suggested range, for example, 57 ± 2 mV for a solution temperature between 20 °C and 25 °C. Slope is defined as the change in mV observed when the concentration changes by a factor of 10. To a 250-mL beaker add 100 mL of deionized water and 1 mL of low-level ISA. Place the beaker on a magnetic stirrer and a clean stir bar in the beaker and begin stirring at a moderate and constant rate. With the meter in the mV mode, lower the electrode tip(s) into the solution. Using a volumetric pipette, add 1 mL of 1000 mg/L chloride standard solution to the beaker. Once the reading is stable, record the reading. Using a volumetric pipette, add 10 mL of 1000 mg/L chloride standard solution to the beaker. Once the reading is stable, record the reading. Input the data into the FDOT chloride software (Figure 2) to get the mV difference between the two readings. If the difference is outside the manufacturer's suggested range, refer to the troubleshooting instructions in the electrode manual.

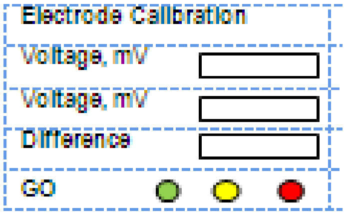


Figure 2. Electrode calibration input and output data fields.

7.5 Blank Sample: Daily at the start of sample analyses and for every 24 analyses (8 samples), obtain the chloride titration end point for deionized water amended with ISA. To 100 ml of deionized water in a 250 ml beaker, add 1.0 ml of low-level ISA. Place the beaker on the magnetic stirrer, and a clean stir bar in the beaker. Rinse the electrode(s) with deionized water and pat dry with lint-free tissue. Immerse electrode(s) in the solution. Stir the solution at a moderate and constant speed. Add 1.0 ml of 0.01 N $AgNO_3$ titrant and record the potential. This potential is hereafter referred to as the scaling potential. Make four 0.5 ml additions of titrant, recording the potential and total volume of titrant after each increment. After all titrant additions have been made, remove the electrodes, rinse them with deionized water, and pat them dry with lint-free tissue. Using the FDOT chloride software, enter the blank data in the space provided (Figure 3). Once the data are entered, the program will indicate the end point for the blank and whether or not it is within the acceptable range. If the intercept does not fall between -0.1 ml and +0.1 ml, the software will indicate the failure. Likewise, the end point for the blank must be within the upper control limit (UCL) and lower control limit (LCL) based on a sequential record of at least 20 blank chloride end points, or the software will indicate a failure. If failure is indicated and data entries are correct, perform the appropriate electrode maintenance per the manufacturer recommendations and then rerun the blank. If samples are run with 0.1 N $AgNO_3$, determine the blank chloride end point with 0.1 N $AgNO_3$ as well.

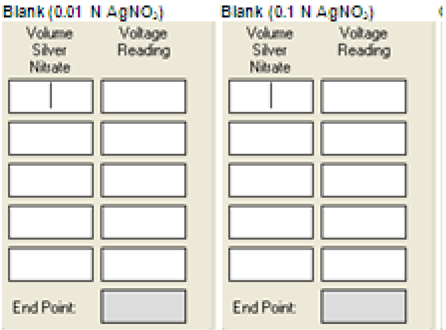


Figure 3. Blank input data fields.

7.6 Chloride Check Standard: Daily at the start of sample analyses and for every 24 analyses (8 samples), obtain the chloride titration end point for a 3 mg/L (ppm) chloride standard. Using a volumetric pipette, pipette 3 mL of 100 ppm chloride standard solution into a 100-mL volumetric flask and add de-ionized water to bring up to volume. Transfer the contents of the volumetric flask to a 250-ml beaker and add 1 ml of low-level ISA. Place the beaker on the magnetic stirrer, and a clean stir bar in the beaker. Rinse the electrode(s) with deionized water and pat dry with lint-free tissue. Immerse electrode(s) in the solution. Stir the solution at a moderate and constant speed. Add 0.01N $AgNO_3$ titrant in 0.5-ml increments until the scaling potential determined in Section 7.5 is just exceeded. Record the total volume of titrant and the potential. Make four more 0.5 ml additions of titrant and record the potential after each addition. Remove the electrodes, rinse them with deionized water, and pat dry with lint-free tissue. Enter the volume and potential data in the FDOT computer software (Figure 4). After blank correction, the observed concentration should be within 5% of the chloride standard concentration and within the upper control limit (UCL) and lower control limit (LCL) based on a sequential record of at least 20 check standard chloride end points; otherwise, the software will indicate a failure. If failure is indicated, prepare fresh reagents as necessary and test again.

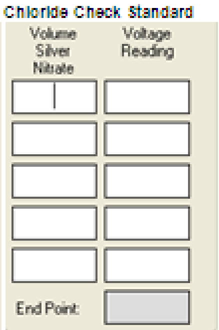


Figure 4. Chloride check standard input data fields.

7.7 Sample Chloride Determination: Empty the contents of one of the 100-ml volumetric flasks prepared in Section 7.1 into a 250-ml beaker. Place the beaker on the magnetic stirrer, and a clean stir bar in the beaker. Rinse the electrodes with deionized water and pat dry with lint-free tissue. Immerse electrode(s) in the solution. Stir the solution at a moderate and constant speed. If the potential exceeds 200 mV (90 mV for combination electrodes) proceed with the test, otherwise redo blank as indicated using 0.1 N $AgNO_3$. In addition, use 0.1 N $AgNO_3$ anywhere the method asks for 0.01 N $AgNO_3$. Add 0.01 N $AgNO_3$ titrant in 0.5-ml increments until the scaling potential determined in Section 7.2 is just exceeded. Record the total volume of titrant and the potential. Make four more 0.5 ml additions of titrant and record the potential after each addition. Remove the electrode(s), rinse with deionized water, and pat dry with lint-free tissue. Enter the volume and potential data in the space provided by the computer program for replicate A (Figure 5). Repeat the procedure for the other two replicates (B and C) using the same $AgNO_3$ normality used with replicate A. Enter the volume and potential data in the computer program for replicate B and C (Figure 5). Check the block on the entry page (not shown) to indicate if samples were run with the cement LCS added. The computer program will subtract the contribution of chloride from the cement LCS from the total chloride to obtain the chloride concentration of the aggregate material.

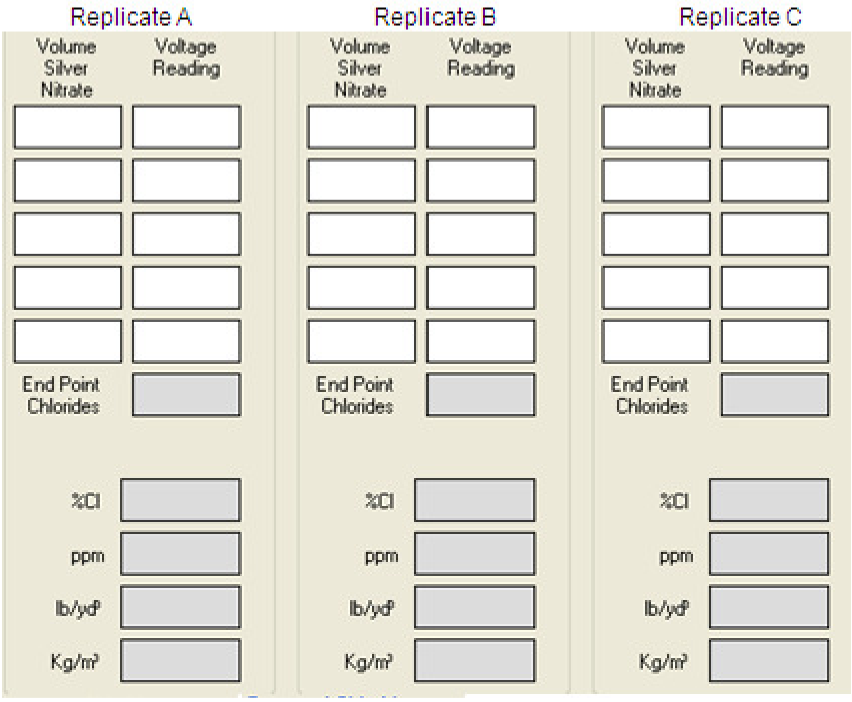


Figure 5. Sample replicate input data fields.

7.8 Laboratory Control Sample (LCS): One for every 24 analyses (8 samples), run one replicate of a LCS by the procedures described in Sections 7.1 and 7.7; alternating between concrete and cement LCS. Enter the volume and potential data in the FDOT computer software (Figure 6). After blank correction, the observed concentration should be within the upper control limit (UCL) and lower control limit (LCL) based on a sequential record of at least LCS chloride end points; otherwise, the software will indicate a failure. If failure is indicated, prepare fresh reagents and test again.

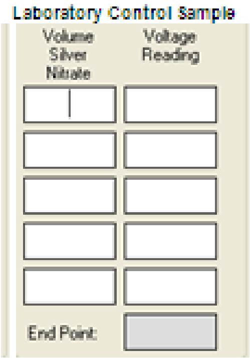


Figure 6. Laboratory Control Sample (LCS) input data fields.

8. CALCULATIONS

8.1 The computer software will perform all the calculations required based on the normality, unit weight, and sample mass (Figure 7). Once all the pertinent data have been entered into the appropriate field, the results are displayed for the sample (Figure 8).

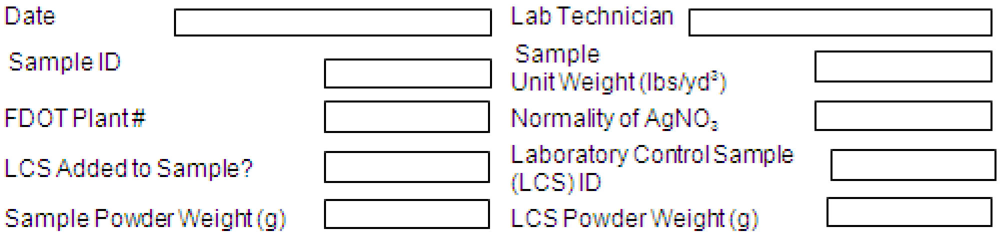


Figure 7. Sample information.

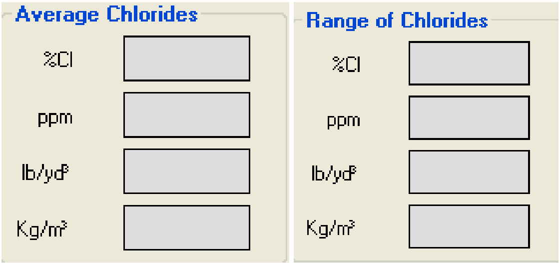


Figure 8. Calculated results.

9. DISPOSAL OF PROCESS WASTE

9.1 Disposal of Process Waste: Dispose of process waste in accordance with the most stringent of local, state, or national regulations.