SHRP-S-328

Condition Evaluation of Concrete Bridges Relative to Reinforcement Corrosion

Volume 6: Method for Field Determination of Total Chloride Content

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Strategic Highway Research Program
National Research Council
Washington, DC 1993

SHRP-S-328
ISBN: 309-05262-9
Contract C-101

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September 1992

Key words:
chloride content
chloride profile
concrete bridges
on-site testing
reinforcement corrosion
specific ion probe

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IM/NAP/293

Acknowledgments

The research described herein was supported by the Strategic Highway Research Program (SHRP). SHRP is a unit of the National Research Council that was authorized by section 128 of the Surface Transportation and Uniform Relocation Assistance Act of 1987.

For help in arranging the traffic control and access to the sampling locations, the authors are especially indebted to Richard Kessler and Ron Powers of the Florida Department of Transportation, Howard Newlon, Jr. and Dallas Cranford of the Virginia Department of Transportation, Gary Hoffman and Jim Seksinsky of the Pennsylvania Department of Transportation, and Lee Schuchardt and Gerald Anderson of the Wisconsin Department of Transportation. Without their cooperation this research could not have been accomplished.

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Abstract

Chloride-induced corrosion of the reinforcing steel is recognized as a primary factor contributing to concrete bridge deck deterioration. This report deals with the selection of a method and the development of detailed procedures to accurately measure the chloride content of reinforced concrete in the field.

Specific ion probe, spectrophotometer, digital titrator, and Quantab titrator strips were the methods investigated. Results from laboratory procedures and an evaluation based on cost, speed, accuracy, and level of required expertise indicated that the specific ion probe was more suitable for use in the field than the other methods selected.

Field validation testing undertaken to substantiate laboratory findings was accomplished by evaluating samples from bridges located in different environmental exposures. Bridges in Pennsylvania, Florida, Wisconsin, and Virginia were tested for chloride content. The determined chloride contents correlated very highly with the standard laboratory method (potentiometric titration--AASHTO T260-84) that was run on companion specimens.

Guidelines were produced for the instrumentation, digestion solution, and test procedure. To evaluate the enhanced procedures, manufactured-precontaminated concrete samples were tested in the laboratory along with samples collected from Florida, Pennsylvania, Wisconsin, and Virginia. Variance methods were used to determine the effects of multiple operators for a fixed procedure, and a detailed test procedure, in American Society of Testing and Materials (ASTM) format, was prepared.

Executive Summary

The standard method for determining the chloride content of concrete--potentiometric titration in the laboratory (AASHTO T260-84)--is arduous, time-consuming, and expensive. Since the 1960s many alternative methods have been developed, but none have been thoroughly evaluated for applicability and accuracy.

A detailed search of the technical literature produced four candidate methods for consideration: the specific ion probe, spectrophotometer, digital titrator, and Quantab titrator strips. All of these methods (as well as the standard potentiometric titration procedure) require the acquisition of drilled powder samples. Therefore, an efficient system for sample acquisition was also developed in this research. Extensive laboratory evaluations identified the specific ion probe as the best alternative based primarily on technical performance and secondarily on cost, speed, and ease of operation.

Laboratory studies on the effects of sample and test variables on test results revealed that cement content had no effect, but that correction factors had to be applied to correct for variations in reaction temperature.

Field validation studies were undertaken in order to evaluate the techniques and procedures used in adapting the specific ion probe method for performing chloride determinations in the field. Four bridges were sampled in Pennsylvania, and three each in Florida, Wisconsin, and Virginia, providing a nationally representative range of chloride exposure environments. The method worked exceedingly well, producing chloride content results that correlated very highly with the standard potentiometric titration procedure (AASHTO T260-84) at production rates per operator of 40 to 50 specimens per day in the field or 70 to 80 in the laboratory.

The specific ion probe system used in the preliminary study employed proprietary solutions for specimen preparation and testing, and unknown instrument configurations. Also, the calibration ranges were not sufficient, resulting in loss of accuracy at high chloride contents. Therefore, the following supplemental studies were carried out:

- Commercially available potentiometers were evaluated for accuracy. The primary qualification was a rugged potentiometer, for laboratory as well as field usage, with a resolution of 1 mV;

- Commercially available specific ion probes used in determining chlorides were investigated. The Orion probe proved to be the only durable probe for the test procedure;

- A digestive solution suitable for concrete was developed and evaluated. The solution developed is an acidic solution with a defoaming agent;

- The calibration solution ranges were expanded to incorporate higher percentages of chloride. The increased ranges improved the accuracy of the reading. Additional improvement was achieved through the dilution for the sample in the stabilizing solution;

- The accuracy of the instrument was determined using pure saline solution. The test displayed a workable range for the probe, which supported the use of a stabilizing solution;

- The accuracy of the procedure was assessed with actual chloride-contaminated concrete samples. The procedure provided high correlations with the AASHTO method for samples from the laboratory and four different states; and

- The accuracy of the procedure with multiple operators was evaluated. Different operators produced similar results.

Finally, a detailed test procedure, in ASTM format, was prepared and is presented in Volume 8, "Procedure Manual," of this report series.

1

Introduction

Needs

The deterioration of concrete bridges in the United States is a monumental problem. The seriousness of the deterioration was first noted in the early 1960s (*1,2*) and has grown since. The financial consequences of the problem associated with the corrosion of the reinforcing steel in concrete bridges was recognized in the early 1970s. The Federal Highway Administration (FHWA) estimated the cost of bridge deck repairs at $70 million per year in 1973 (*3*). By 1975, the estimate for bridge deck repairs was increased to $200 million per year (*4*). In 1981, a report published by the U.S. General Accounting Office (*5*) covering some 514,000 of the nation's 566,000 bridges estimated the rehabilitation/replacement at $33.2 billion. About one-half, or $16 billion, is due to the corrosion of steel in concrete. The problem has been steadily growing in magnitude; more recent projections presented in the final report *Strategic Highway Research Program Research Plans* estimate the liability of corrosion-induced deterioration in bridges at $20 billion, increasing by a rate of $.5 billion annually (*6*).

Many of the studies pertaining to concrete bridge deterioration address the corrosion of the reinforcement steel in concrete. The corrosion of reinforcing steel in concrete is influenced by many factors: concrete permeability (w/c ratio); consolidation of the concrete during placement; the type of cement; cover depth above the reinforcement steel; relative humidity; and the ions present at the steel surface (*7*).

In reinforced concrete, a protective layer is provided in the alkaline environment and passivity (resistance to corrosion) exists so long as the pH remains high in the concrete in contact with the surface of the reinforcement steel. Two mechanisms can destroy the passive layer (*8*). The first mechanism is the reduction of alkalinity by leaching of water or a reaction with carbon dioxide or some other acidic material to partially neutralize the passive layer. The second mechanism is an electrochemical reaction of chloride ions in the presence of oxygen.

The reaction products formed are much larger than the volume of steel, and, ultimately, the pressures induced cause rupture in the concrete above the reinforcing steel (*9*). Once the concrete surface has cracked the corrosion rate increases due to the increased availability of oxygen to depolarize cathodic areas.

The primary sources of the chloride ion detected in concrete bridges are deicing salts, sodium and/or calcium chloride, and sea water spray, which infiltrates into the concrete through cracks or by diffusion (*10*). Chloride may also be present in the mixing water, admixtures, or aggregates used in the concrete mixture. A typical bridge will receive from 0.25 to 1.0 lb/ft^2 of deicer salt per winter (*10*). These chlorides can penetrate bridge structures through cracks, faulty joints, and diffusion through the concrete itself to initiate corrosion. The "bare pavement" policy of the 1960s increased the amount of deicing salts applied each winter from 2 to 9 million tons in the snow belt states (*11*). This increased the severity of the corrosion problem and accelerated the need for strategies to rehabilitate and replace deteriorated bridges.

To implement these strategies and new anti-corrosion methods (cathodic protection, overlays, and epoxy-coated reinforcing bars), it is necessary to be able to determine the extent of chloride contamination in bridge components. Thus, a field test procedure for determining the extent of chloride contamination is needed. A successful field procedure must meet several criteria. It must accurately determine existing chloride contamination levels; it must be simple enough for technicians to perform in the field; and it should not be too time- or equipment-intensive.

Objectives and Scope

The ultimate objective of this study was to develop an economic, reliable field method of measuring the chloride content of bridge components. The developed method would be used to assess the existing corrosion condition and predict the future corrosion condition of reinforced concrete bridge components.

To satisfy the objective of this study, a state-of-the-art literature review was first carried out in order to identify different chloride measurement methods. The identified methods were investigated to determine their applicability relative to the measurement of chloride content of bridge components in situ or in powdered samples. The evaluation criteria included speed, accuracy, level of expertise required, cost (equipment and samples analyzed), and equipment limitations. The most feasible method was chosen for field validation. An intensive field study was conducted to validate the laboratory results. A correlation study of the developed procedure and the standard potentiometric titration method was performed. The effects of temperature and cement content on the developed procedure were investigated as was a statistical base to determine the instrument and operator variability. The method was field-validated using drilled concrete samples taken from bridges in Virginia, Pennsylvania, Wisconsin, and Florida.

Research Approach

The research approach employed in the pursuit of the objectives of the research consisted of the following steps:

- Identification of technically feasible methods;

- Selection of one of the technically feasible methods (by means of laboratory screening tests) for further development;

- Validation of the selected method under field conditions;

- Enhancement of the selected method, addressing shortcomings uncovered during the laboratory and field validation testing.

2

Background

Literature Review

Manual and computer data base searches were performed to identify test methods used to determine the chloride content of concrete. In addition, sources of information containing the chloride content for various bridges within the United States were identified: the Engineering Indexes Annual from 1955 to 1988, HRIS abstracts from 1979 to 1987, Chemical Abstracts, and government documents were searched.

Methods used to determine the chloride ion content of concrete may be classified as nondestructive and destructive techniques. Nondestructive techniques include the dual neutron-gamma ray and the neutron-gamma ray spectroscope. Destructive methods, requiring a drilled, powdered sample, include the American Association of State Highway and Transportation Officials (AASHTO) Standard Method T260-84 (potentiometric titration method) X-ray fluorescence, gas chromatograph, Quantab chloride titrator strips, specific ion electrode, spectrophotometer, and argentometric digital titrator. The following sections present the initial evaluation of the test methods examined in selecting the feasible methods for laboratory evaluation study.

Dual Neutron-Gamma Ray Technique

The dual neutron-gamma ray technique was developed for FHWA by Columbia Scientific Industries (*12,13*). The instrument can measure chloride content with respect to depth, with detection limits of 0.04 to 0.08 lb Cl/yd^3 (0.02 to 0.05 kg/m^3) and depth resolutions of 0.40 to 8 in. (1 to 20 cm), depending on the calibration model. Calibration models would have to be developed for specific types of bridges (e.g., concrete or steel beams, varying deck thickness, varying overlay thickness, and coastal or inland bridges) (*13*). The choice of the wrong calibration model (Cl depth distribution model) will result in significant measurement errors. The method is fast, taking two to three measurements per hour with a 10-minutes data acquisition time. Instrument operation is straightforward and requires little training. However, instrument calibration and setup must be done by qualified scientists. Although operational costs are relatively low, capital costs are very high. Also, the equipment is very large and is mounted on a self-contained vehicle and thus would be limited to use on bridge decks. However, the instrument can be used to measure the chloride content of 0.66- to 0.88-lb (300- to 400-g) powder concrete samples with a 0.25-in. (6.4 mm) maximum particle size, taken from other instrument-inaccessible bridge members.

Further investigation of the dual neutron-gamma ray technique was not conducted in this study for reasons of its cost, number of required chloride distribution calibration models, portability limitations, and technical qualifications of setup and calibration personnel.

Neutron-Gamma Ray Spectroscopy

Neutron-gamma ray spectroscopy uses a californium-252 neutron source for composition measurements with a high-resolution, high-purity germanium detector rather than an NaI (Tl) crystal gamma-ray detector (*14-16*). The instrument has been used to measure the relative difference with regard to surface position of the chloride content of a masonry wall by normalizing the chloride intensities to the value of silicon (Cl/Si ratio). The procedure assumes that the value of silicon remains relatively constant throughout the material.

Some of the characteristics of the current neutron-gamma ray spectroscope are presented below:

1. The apparatus for building walls consists of a neutron source, liquid nitrogen cooled Ge(HP) gamma-ray detector, amplifier, multichannel analyzer, tape and chart recorder, and readout unit. The apparatus is awkward to transport and set up on building walls. However, smaller portable versions of the multichannel analyzer, amplifiers, and tape deck are commercially available. Similarly, small-sized liquid nitrogen flasks are available. These improvements would improve the portability of the apparatus.

2. For measurements of building walls, the neutron source is placed on one side of the wall and the gamma-ray detector is placed directly opposite the source on the other side of the wall. This measurement setup cannot be used on most bridge components. However, measurements can be made with the detector and source on the same flat surface if a shield is provided for the source and detector. The increased weight would significantly reduce the portability of the apparatus.

3. The instrument measures the resulting gamma rays from a hemispherical volume with a radius of 6 to 8 in. (15 to 20 cm) around the detector and thus measures the average gamma-ray response for the volume of about 460 to 1,100 in^3 (7,540 to 18,030 cc).

4. The instrument detects relative differences between average chloride contents because no general linear relation exists between the intensity and the concentration of an element (*15*). To measure absolute values, the development of calibration standards would be required for various normalized chloride contents (normalized to silicon). Thus, calibration standards would have to be developed for varying of silicon and chloride contents. In addition, the presence of iron and water also influences intensity. Therefore, calibration standards regarding the influence of these elements must be developed. In that it measures the average chloride content of a volume of concrete, this technique may be of limited value to the application of measuring the chloride content of reinforced concrete bridges because it can only measure the magnitude of chloride content, not changes of 30 to 40 percent (communication with Jacob I. Tromba, 1988). Thus, one may be unable to distinguish the variations in chloride distribution, particularly since the measured volume is hemispherical.

5. The cost of the equipment is on the order of $100,000, and skilled technicians are required to maintain the equipment (*16*). In addition, because each bridge or group of bridges may require some adaptation, the apparatus may be most productive when operated by specialists with a knowledge of nuclear physics. It has been suggested that the technique may best be used through the services of specialized consulting firms (*16*).

Recently, the National Science Foundation (NSF) awarded the Goddard Space Flight Center a contract to investigate the development of calibration models for neutron-gamma ray spectroscopy. Initial results seem promising (communication with Jacob I. Tromba, 1988). Given the current state of development of the technique, the apparent portability problems, calibration requirements, and cost, this technique was not investigated further in this study.

X-Ray Fluorescence and Gas Chromatography

X-ray fluorescence and gas chromatography analysis methods of powder samples offer no advantage over other powder analysis methods because of the related power requirements (X-ray fluorescence requires approximately a 100-kV source), costs (between $25,000 and $100,000 for equipment only), and level of required expertise. These limitations would restrict the use of the instruments to the laboratory. Therefore, the instruments were not evaluated further.

Quantab Chloride Titrator Strips

Quantab chloride titrator strips are simple and fast to use and are applicable to field measurement techniques of powder samples. However, some problems have been encountered in interpreting the results. The National Ready Mixed Concrete Association has developed a method for measuring the chloride ion content of freshly mixed concrete using Quantab titrators (*17*). The method has not been standardized nor has it been subjected to multilab cooperative testing to derive its precision. However, some additional investigation was conducted in this study because of the relatively low cost and simplicity of the method.

A simplified procedure for the Quantab method was also developed by the Building Research Station, Garston, Watford (U.K.), for analyzing the chloride content in portland cement concrete (*18*). The developed analysis procedure for the Quantab titrator strips consists of an acid digestion of a 5.0-g sample of powdered concrete. Fifty ml of 1N nitric acid solution were used to digest the sample, followed by neutralization of the acid using 5.0 g of anhydrous sodium carbonate. Chloride concentration of the sample was then determined using the Quantab titrator strips.

Argentometric Digital Titration

The Building Research Station, Garston, Watford (U.K.), also developed a simplified procedure for chloride determination in portland cement concrete using the Hach (argentometric) test method. In this procedure, the 0.175-oz (5-g), powdered concrete sample is acid-digested with nitric acid. After appropriate sample preparation, it is titrated from a bright yellow to faint reddish brown color and the number of digits required (using the digital titrator) to complete the titration is recorded (*18*).

The techniques developed by the Building Research Station were proposed methods to obtain preliminary results for the chloride content in portland cement concrete. Minimum expertise was required in obtaining reproducible results at the site or other "convenient places." Both procedures were noted for having less accuracy than standard laboratory procedures. Consequently, use of the Quantab method and the argentometric (Hach) test procedures was recommended as a screening process to identify chloride-contaminated samples that require a more detailed analysis. The results could also be used as a justification for the additional expenditure associated with the laboratory procedure (*18*).

Specific Ion Probe

The development of the specific ion probe method for measuring the chloride content of concrete was first conducted at The Pennsylvania State University (*19*). The procedure was further developed for field use by James Instruments (*20*). The method digests a 0.105-oz (3-g), powered sample in a chloride extraction solution. A combination specific chloride ion electrode connected to a voltmeter is inserted into the sample mixture, and the millivolt reading is recorded. The chloride content is determined by using a calibration equation, which in turn is determined every time the instrument is turned on.

Spectrophotometer

The spectrophotometric method compares the color difference of a chloride-extracted mixture with a standard reference solution. The chloride content is a direct digital readout in ppm (*21*).

Promising Approaches

Based on the initial equipment costs, level of expertise required to use the equipment, ruggedness for field use, portability, and accuracy, the specific ion probe, spectrophotometer, digital titrator, and the Quantab titrator strips were selected for further laboratory analysis for accuracy of results compared to the standard potentiometric titration method. The standard method (potentiometric titration--AASHTO T260-84) is too costly and complex and not sufficiently rugged for field use. The direct measurement of chloride content in a drill hole using a specific ion electrode was excluded because it is applicable only to horizontal surfaces (*22*), and, if a hole is to be drilled, little advantage can be realized over the powder sample measurement method.

The details of the four promising methods, along with the standard laboratory method (potentiometric titration) are presented in Appendix A.

3

Preliminary Laboratory Evaluations

Specimen Preparation

The laboratory investigation of the four selected test methods evaluated three things: the accuracy of the test method as compared to the standard test method; the effects of cement content; and effects of changes in temperature on the performance of the selected test method. The accuracy of the test method was used as one of the criteria for the selection of the field test method. Prior to field validation, the effects of cement content and temperature on the selected test method were determined. For the accuracy, cement content, and temperature tests, concrete specimens 1 x 1 ft x 6 in. (30 x 30 x 15 cm) were cast at 10 chloride contamination levels. Specimens were cast at 0.0, 0.2, 0.4, 0.8, 1.6, 3.2, 6.4, 8.6, 10.8, and 12.8 Cl lb/yd^3 (0.0, 0.1, 0.2, 0.5, 1.0, 1.9, 3.8, 5.1, 6.4, and 7.6 kg/m^3, approximately) of concrete using a sodium chloride solution as additive. The characteristics of the concrete mixtures are presented in Table 3-1. A rotary hammer drill with a 3/4-in. (19-mm) carbide drill bit was used to sample each of the concrete slabs. The extracted powder from the multiple drill holes in a single contaminated slab was combined, dried, and sieved over a No. 50 (300 μm) sieve, and the retained 50 (300 μm) sieve material was discarded.

The standard potentiometric titration procedure (*23*), AASHTO T-260-84, was used as the basis for comparison of the chloride content of the test samples for each of the four selected methods. The procedure used is presented in Appendix A. Four samples from each of the 10 chloride contamination levels were analyzed using the standard method (and the 4 selected methods). The results obtained using the standard potentiometric titration method were compared with the known amounts of chloride added to each specimen. The amount of

Table 3-1. Properties of the concrete mixtures.

Batch No.	w/c	Cl Content (lb/yd^3)	Unit Wt. (lb/ft^3)	Air (%)	Slump (in.)	*Compressive Strength (psi)	
						7 day	28 day
C-0	.47	0.0	146.2	5.1	6 1/2	3600	4810
C-1	.47	.2	146.7	5.4	3	4250**	5250
C-2	.47	.4	146.7	5.2	3	4340**	5050
C-3	.47	.8	145.4	5.6	4 3/8	4140**	4910
C-4	.47	1.6	147.0	5.0	4	4350**	4810
C-5	.47	3.2	147.6	5.0	3 5/8	3700**	5240
C-6	.47	6.4	147.3	5.7	3 3/4	3700**	4900
C-7	.47	8.6	148.8	4.5	7 1/4	3960	4600
C-8	.47	10.8	148.3	5.2	4	4380	5080
C-9	.47	12.8	146.5	5.4	4 3/4	3690**	4990
DC-0	.40	0.0	147.6	6.0	2 1/4	5140	6170
DC-1	.40	.2	144.5	6.6	5 1/2	4540	5890
DC-2	.40	.4	147.0	5.5	3 3/4	5090	6400
DC-3	.40	.8	147.8	5.1	5 1/2	4850	6610
DC-4	.40	1.6	148.8	5.6	3	5130	6170
DC-5	.40	3.2	146.4	6.0	7	4860	6140
DC-6	.40	6.4	144.1	7.1	8	4940	5780
DC-7	.40	8.6	143.1	7.1	8 3/4	4840	5700
DC-8	.40	10.8	142.7	8.0	8	4840	5550
DC-9	.40	12.8	147.4	6.0	6 1/2	4820	5740
EC-0	.50	0.0	145.5	5.6	3 1/2	3750	4850
EC-1	.50	.2	146.0	5.7	3 1/2	3790	4690
EC-2	.50	.4	146.1	6.0	3 3/4	3870	4830
EC-3	.50	.8	146.6	6.0	3 3/4	3710	4580
EC-4	.50	1.6	146.6	5.2	3 3/4	3620	4480
EC-5	.50	3.2	147.0	5.3	4 1/8	3610	4230
EC-6	.50	6.4	146.3	5.5	4	3510	4290
EC-7	.50	8.6	146.8	5.6	4	3720	4250
EC-8	.50	10.8	146.2	5.4	5	3540	4440
EC-9	.50	12.8	146.8	5.6	4	3520	4610

* Average of two cylinder tests.
**Indicate 8-day strength results.

background chloride in each specimen was estimated to be the average of four tests on specimen C-0 (0.02025 percent), as illustrated in Table 3-2. The Wilcoxon Signed Rank procedure (*24*) for paired data was used to determine if the amount of chloride measured using the potentiometric titration less the amount of chloride added was equivalent to the amount of background chloride. The test results presented in Table 3-2 were used for the comparison.

The results of the Wilcoxon Signed Rank procedure suggests that there is sufficient evidence to indicate that the difference in the amount of chloride added and the amount of chloride measured in the specimens is more than the amount of background chloride as determined by testing four samples from specimen C-0 for chloride. In essence, the results of this analysis indicate there were errors associated in adding chloride to the 10 specimens, variations in the amount of background chloride present in the aggregate materials or mixing water in each specimen, and/or different amounts of aggregates present in each sample (resulting in different values for the amount of chloride present) as a result of the sampling procedure.

Because the results of the Wilcoxon Signed Rank analysis procedure were somewhat inconclusive, a regression analysis procedure was performed to determine if a relationship exists between the difference in the amount of chloride added and the amount of chloride measured in the specimens versus the amount of chloride added to the concrete. The following equation represents the results obtained from a regression analysis:

$$\mathrm{ACT\text{-}ADD} = 0.0160 + 0.103\ \mathrm{ACTCL} \tag{3-1}$$

where

ACT-ADD = amount of chloride measured minus the added chloride, and
ACTCL = the amount of chloride added.

The results of the analysis of variance indicate that the error sum of squares for the predicted values is nearly as great as the error sum of squares for the regression. In summary, the analysis of the results indicate that the total variation between the difference or background chloride and the actual amount of chloride added is not entirely due to errors associated with measuring or adding chloride to the specimens. When incorporating the results of the Wilcoxon Signed Rank procedure with the regression analysis, one may conclude that the total variation in the results observed is not entirely associated with operator and instrument errors in adding chloride to the 10 specimens. In other words, the amount of background chloride present in the aggregate materials or mixing water varies in each specimen or from batch to batch when mixing concrete, or different amounts of aggregates were present in each sample as a result of the sampling procedure used.

Table 3-2. Comparison of the potentiometric titration results and amount of chloride added.

Specimen	Measured Chloride (%Cl)	Added Chloride (%Cl)	Measured Added Difference (%Cl)
C-0	.023	.000	.023
C-0	.018	.000	.018
C-0	.020	.000	.020
C-0	.020	.000	.020
C-1	.026	.005	.021
C-1	.027	.005	.022
C-1	.027	.005	.022
C-1	.021	.005	.016
C-2	.032	.010	.022
C-2	.028	.010	.018
C-2	.032	.010	.022
C-2	.033	.010	.023
C-3	.049	.020	.029
C-3	.045	.020	.025
C-3	.049	.020	.029
C-3	.049	.020	.029
C-4	.064	.040	.024
C-4	.063	.040	.023
C-4	.062	.040	.022
C-4	.060	.040	.020
C-5	.111	.080	.031
C-5	.115	.080	.035
C-5	.115	.080	.035
C-5	.112	.080	.032
C-6	.198	.161	.037
C-6	.191	.161	.030
C-6	.189	.161	.028
C-6	.191	.161	.030
C-7	.222	.214	.008
C-7	.222	.214	.008
C-7	.221	.214	.007
C-7	.220	.214	.006
C-8	.330	.270	.060
C-8	.330	.270	.060
C-8	.329	.270	.059
C-8	.328	.270	.058
C-9	.388	.324	.064
C-9	.396	.324	.072
C-9	.386	.324	.062
C-9	.386	.324	.062

Evaluation of the Promising Approaches

Specific Ion Probe, Model Cl 500

The testing procedure developed by James Instruments, Inc. *(20)* involves calibrating the specific ion electrode using three known standards by plotting the electrometer readings (millivolts) versus percent chloride on semilog graph paper. The powdered material is placed in an ampoule and compressed to a level corresponding to a red indicator line. The sample is then added to a premeasured amount of the "chloride extraction liquid" and shaken for 15 seconds. The electrode is submerged in the solution and the electrometer reading is plotted. The corresponding chloride content of the sample may then be read directly from the calibrated graph.

To determine the relationship between the chloride contents of the calibration liquids provided by James Instruments, Inc. and the readings obtained on the electrometer, a deviation from the recommended procedure was used. This deviation involved a regression analysis of the results, and was used instead of determining the relationship graphically, to allow more precision in the results of the analysis. Results of regression analyses at two different time periods indicate that the estimated value for the slope is significantly different from 0 at the 5-percent level of significance, while the intercept is not. The coefficient of determination, R^2, indicates that 99.8 to 99.9 percent of the variation in the $\log_{10}$ of the percentage of chloride present in each of the three calibration liquids can be predicted from the millivolt readings. The results of the analysis of variance indicate that the error sum of squares for the predicted values is very small, much less than the error sum of squares for the regression.

The readings obtained from the James Instruments' specific ion probe on samples from the test slabs were converted to percent of chloride using the regression equations. The results for the potentiometric titration procedure and the specific ion probe are presented in Table 3-3.

Table 3-3. Comparison of the potentiometric titration and the specific ion probe results at w/c = .47.

Specimen	Potentiometric Titration (%Cl)	Specific Ion Probe	
		Millivolt Reading	Calculated %Cl
C-0	.023	82.0	.012
C-0	.018	82.0	.012
C-0	.020	81.7	.012
C-0	.020	81.8	.012
C-1	.026	60.7	.029
C-1	.027	76.2	.015
C-1	.027	79.1	.013
C-1	.021	72.0	.018
C-2	.032	63.2	.026
C-2	.028	65.8	.023
C-2	.032	64.5	.024
C-2	.033	64.6	.024
C-3	.049	48.4	.048
C-3	.045	47.8	.050
C-3	.049	47.5	.050
C-3	.049	45.5	.055
C-4	.064	39.1	.072
C-4	.063	39.7	.070
C-4	.062	39.6	.071
C-4	.060	39.7	.070
C-5	.111	23.4	.142
C-5	.115	20.2	.163
C-5	.115	21.3	.155
C-5	.112	19.6	.167
C-6	.198	6.1	.299
C-6	.191	6.5	.293
C-6	.189	5.9	.302
C-6	.191	6.4	.295
C-7	.222	-0.2	.368
C-7	.222	-3.0	.413
C-7	.221	-1.6	.390
C-7	.330	-0.1	.366
C-8	.330	-8.1	.510
C-8	.330	-11.6	.590
C-8	.329	-9.2	.534
C-8	.328	-7.6	.500
C-9	.388	-15.2	.749
C-9	.396	-14.7	.733
C-9	.386	-15.5	.758
C-9	.386	-16.4	.788

A regression analysis to determine the relationship between the results from the standard potentiometric titration procedure and the specific ion probe was performed. The regression equation using the specific ion probe for the data presented in Table 3-3 is as follows:

$$\text{TITR\%} = 0.00459 + 0.493\ \text{\%JAM}^{0.8} \qquad (3\text{-}2)$$

where

TITR% = the values for %Cl obtained from the potentiometric titration procedure, and
%JAM = the readings obtained using the specific ion probe.

Results of the regression analysis indicate that the estimated value for the slope is significantly different from 0 at the 5-percent level of significance, while the intercept is not. The coefficient of determination, R^2, indicates that 99.1 percent of the variation in *TITR%* can be predicted from the independent variable $\%JAM^{0.8}$ (millivolt readings converted to percent chloride). The results of the analysis of variance indicate that the error sum of squares for the predicted values is very small in relation to the error sum of squares for the regression.

The regression analysis indicates that a strong relationship exists between the results from the standard potentiometric titration procedure and the results obtained from tests conducted with the specific ion probe. Although the results of the analysis indicate that the value for the intercept is not significantly different from 0 at the 5-percent level of significance, the intercept value obtained from the method of least squares is maintained to reduce the element of bias in the estimates for the predicted values from the standard potentiometric titration procedure. A plot of the results obtained using the specific ion probe as a function of the potentiometric titration results and the 95-percent confidence limits for the prediction interval is presented in Figure 3-1.

Spectrophotometric Method

The DR/2000 spectrophotometric testing procedure developed by the Hach Company (*21*) includes specifying the chloride test procedure and entering the appropriate wavelength for the chloride test. Two sample cells are prepared, one with deionized water and the other with the filtered sample to be analyzed. Two ml of mercuric thiocyanate and 1.0 ml of ferric ion solution are added to each sample and swirled to mix. After mixing, the two samples are analyzed after a 2-minute waiting period. The blank cell is used to zero the

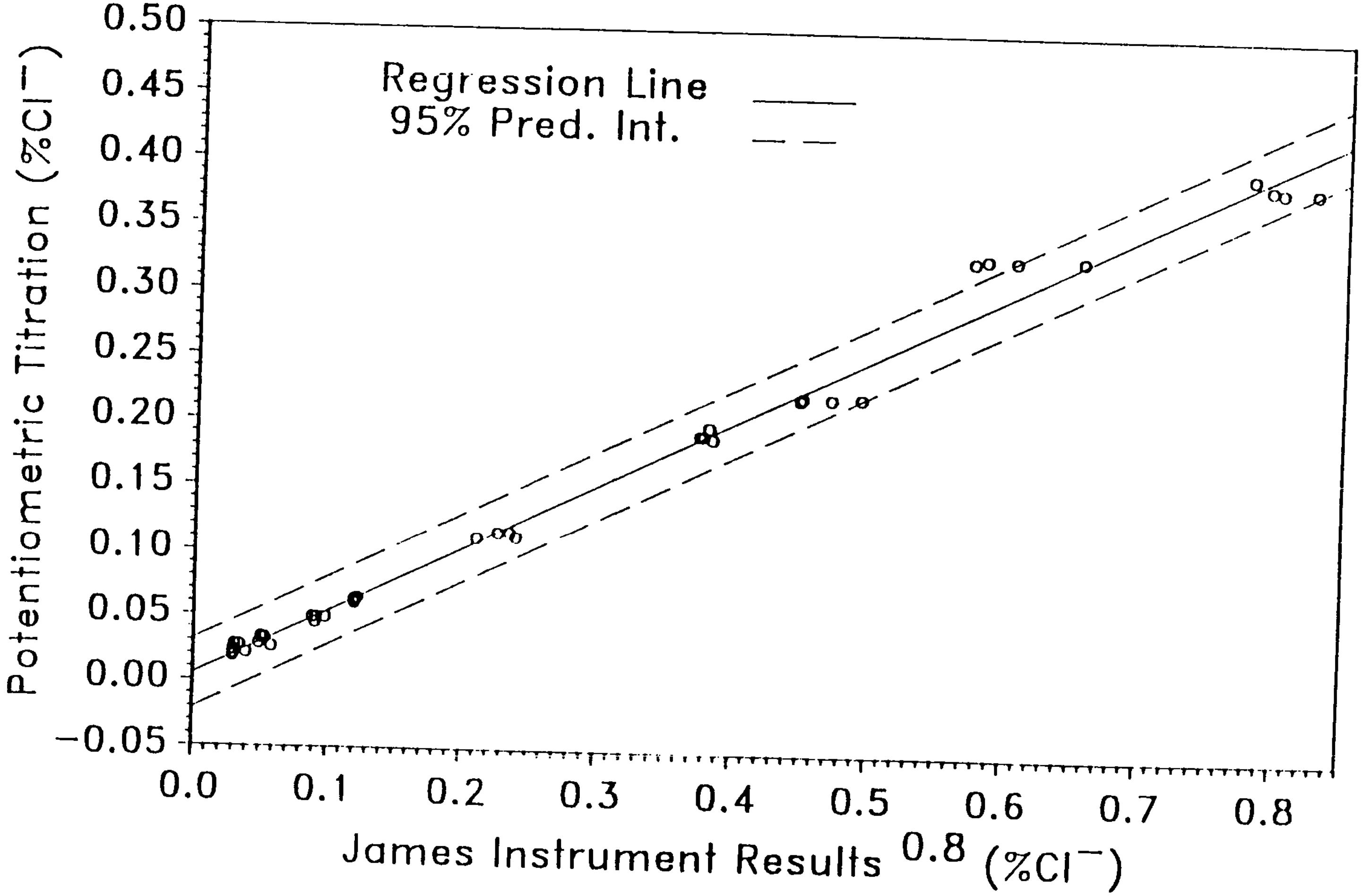


Figure 3-1. Potentiometric titration versus the specific ion probe.

instrument prior to analyzing the sample cell for chloride content. Table 3-4 presents the test results of the 10 concrete chloride ion concentration levels for the DR/2000 spectrophotometer and the standard test method. A regression analysis was performed on the data from Table 3-4. The regression equation for the spectrophotometer is as follows:

$$\mathrm{TITR\%} = -0.00856 + 0.0207\ \mathrm{SPECTRO} \qquad (3\text{-}3)$$

where

TITR% = results from tests using the standard potentiometric titration procedure, and

SPECTRO = results obtained from the spectrophotometer.

Results of the regression analysis indicate that the estimated value for the slope is significantly different from 0 at the 5-percent level of significance, while the intercept is not significant. The coefficient of determination, R^2, indicates that 96.4 percent of the variation in TITR% can be predicted from the independent variable SPECTRO (results from the spectrophotometer). The results of the analysis of variance indicate that the error sum of squares for the predicted values is relatively small compared to the error sum of squares for the regression.

The regression analysis indicates that a strong relationship exists between the results from the standard potentiometric titration procedure and the results obtained from tests conducted with the spectrophotometer. A plot of the spectrophotometer and the potentiometric titration results and the 95-percent confidence limits for the prediction interval is presented in Figure 3-2.

CD-DT Digital Titrator

The analysis procedure for this method, developed by the Hach Company (*25*), involves transferring the sample into an Erlenmeyer flask and diluting it, if necessary, with deionized water. Diphenylcarbazone powder is added and swirled to mix. The sample is then titrated with mercuric nitrate to a light pink color. The number of digits required is used in calculating the chloride content. The results of the chloride tests for the digital titrator and standard method are presented in Table 3-5. A regression analysis was performed on the test results presented in Table 3-5. The regression equation for the digital titrator is as follows:

Table 3-4. Comparison of potentiometric titration and the spectrophotometer results at w/c = .47.

Specimen	Potentiometric Titration (%Cl)	Spectrophotometer Chloride (mg/L)
C-0	.023	1.8
C-0	.018	2.7
C-0	.020	2.3
C-0	.020	2.1
C-1	.026	1.5
C-1	.027	2.3
C-1	.027	1.1
C-1	.021	2.0
C-2	.032	2.0
C-2	.028	2.1
C-2	.032	1.8
C-2	.033	1.8
C-3	.049	2.4
C-3	.045	2.9
C-3	.049	2.1
C-3	.049	2.6
C-4	.064	3.7
C-4	.063	2.8
C-4	.062	2.1
C-4	.060	3.4
C-5	.111	4.8
C-5	.115	6.2
C-5	.115	6.5
C-5	.112	7.9
C-6	.198	9.8
C-6	.191	9.9
C-6	.189	9.7
C-6	.191	9.5
C-7	.222	12.1
C-7	.222	11.7
C-7	.221	11.1
C-7	.220	8.0
C-8	.330	16.0
C-8	.330	16.2
C-8	.329	19.7
C-8	.328	17.7
C-9	.388	15.8
C-9	.396	17.5
C-9	.386	19.1
C-9	.386	18.1

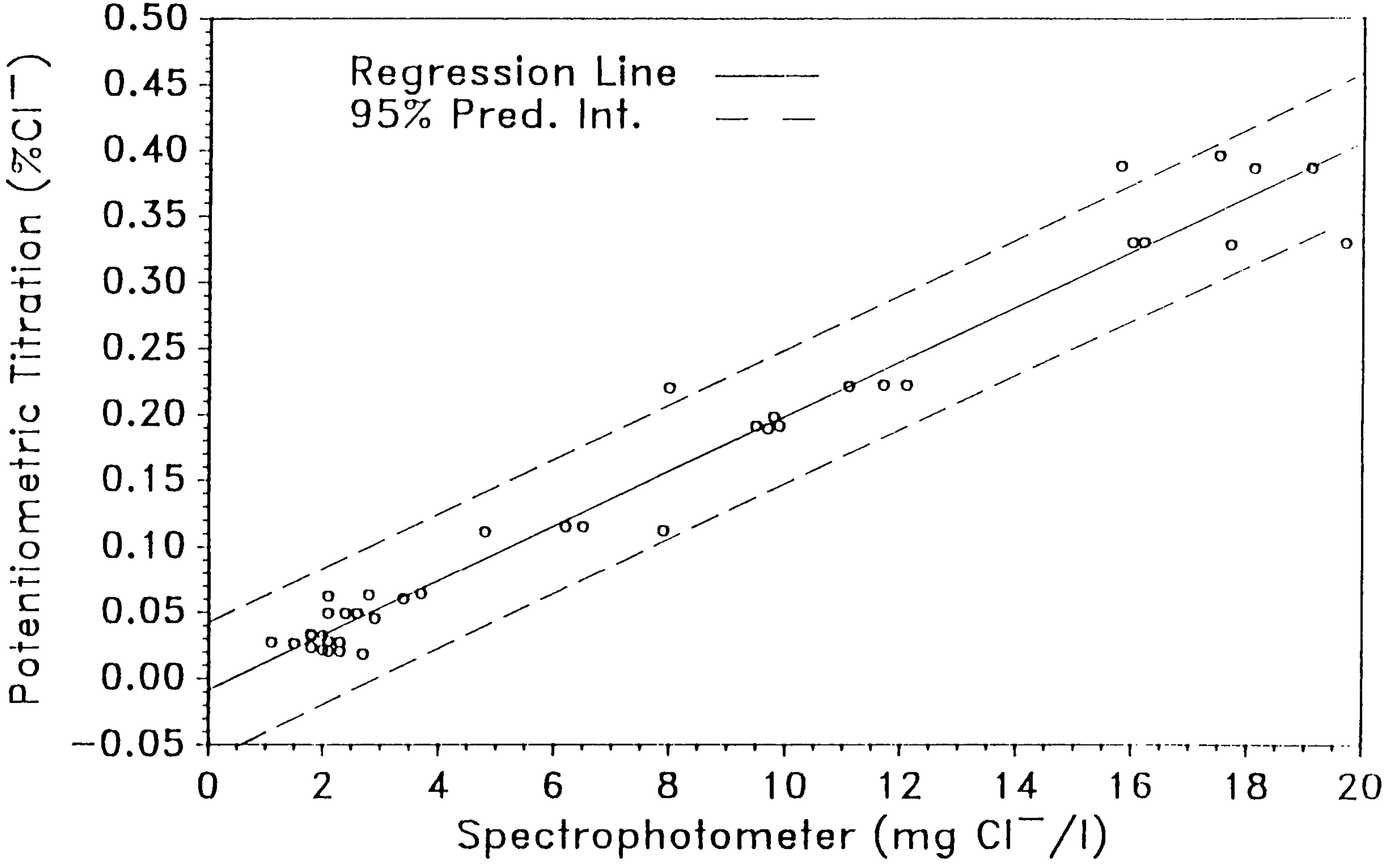


Figure 3-2. Potentiometric titration versus spectrophotometer.

Table 3-5. Comparison of potentiometric titration and the digital titrator results at w/c = .47.

Specimen	Potentiometric Titration (%Cl)	Digital Titrator Chloride (mg/L)
C-0	.023	10.5
C-0	.018	5.0
C-0	.020	6.0
C-0	.020	7.0
C-1	.026	8.5
C-1	.027	11.0
C-1	.027	2.5
C-1	.021	7.0
C-2	.032	10.0
C-2	.028	5.0
C-2	.032	8.0
C-2	.033	8.0
C-3	.049	9.0
C-3	.045	7.5
C-3	.049	13.0
C-3	.049	10.0
C-4	.064	13.0
C-4	.063	14.0
C-4	.062	15.0
C-4	.060	12.0
C-5	.111	25.0
C-5	.115	16.0
C-5	.115	18.5
C-5	.112	22.0
C-6	.198	30.0
C-6	.191	30.0
C-6	.189	32.0
C-6	.191	32.5
C-7	.222	34.0
C-7	.222	31.0
C-7	.221	35.5
C-7	.220	33.0
C-8	.330	52.0
C-8	.330	55.0
C-8	.329	51.0
C-8	.328	50.0
C-9	.388	59.0
C-9	.396	63.0
C-9	.386	55.0
C-9	.386	56.0

$$\mathrm{TITR\%} = -0.0238 + 0.00694\ \mathrm{DIGITAL} \tag{3-4}$$

where

TITR% = the results from the test using the standard potentiometric titration procedure, and
DIGITAL = the results obtained from the digital titrator, also presented in Table 3-5.

Results of the regression analysis indicate that the estimated value for the slope is significantly different from 0 at the 5-percent level of significance, while the intercept is not. The coefficient of determination, R^2, indicates that 98.3 percent of the variation in TITR% can be predicted from the independent variable DIGITAL (readings from the digital titrator). The results of the analysis of variance indicate that the error sum of squares for the predicted values is relatively small compared to the error sum of squares for the regression.

The regression analysis indicates that a strong relationship exists between the results from the standard potentiometric titration procedure and the results obtained from tests conducted with the digital titrator. A plot of the digital titrator as a function of the potentiometric titration results and the associated 95-percent confidence limits is presented in Figure 3-3.

Quantab Titrator Strips

The Quantab titrator strips procedure was developed by Environmental Test Systems, Inc. (*26*). It involves weighing 10.0 g of the sample and adding 90 ml of boiling distilled water, stirring constantly. The sample is stirred for 30 seconds, and after 1 minute it is stirred again for another 30-second period. Filter paper is folded to a cone and placed into the beaker to allow some of the sample to filter through. A Quantab titrator strip is placed in the filtered portion of the sample and is left there until a dark blue color forms at the top of the strip. The reading of the Quantab titrator strip is used in determining the chloride content from a calibrated chart.

The titrator strips were somewhat difficult to read. The change in the color of the Quantab strip to white indicated very low readings, which were considered unrealistic for the amount of chloride present in the samples. As a result, the highest reading that indicated a change in color on the test strip was recorded for the result. The color change was not white but a yellow to a yellowish brown. Because these problems did occur, tests using the procedure for water-soluble chlorides were not completed for all of the specimens.

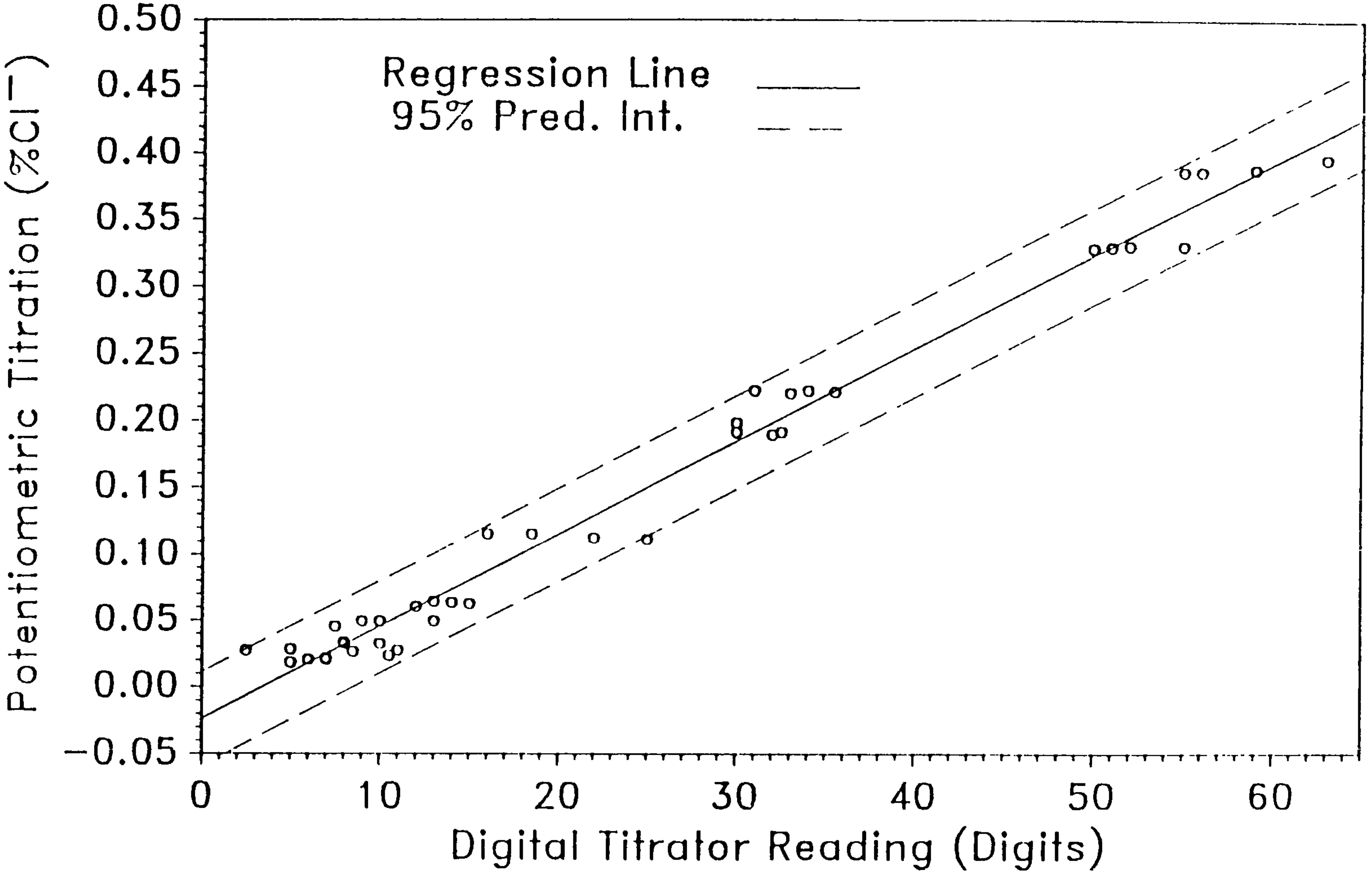


Figure 3-3. Potentiometric titration versus digital titrator.

Four samples from each of the 10 chloride-contaminated concrete specimens were tested for total chloride content (acid digestion procedure) using the Quantab titrator strips. The results obtained using this method are presented in Table 3-6. During this series of tests, the Quantab readings were more distinct and easier to read. The white color on the strip represented higher readings from the previous procedure, indicating that more chloride was being extracted from the sample. However, there were no secondary or partial color changes above the white colored area as observed using the manufacturer's procedure.

Acid-digested samples analyzed using the Quantab titrator strips were compared to the results obtained from the potentiometric titration procedure. In comparing the results, a regression analysis was performed. The most appropriate regression equation for the Quantab titrator strips was found to be:

$$\mathrm{TITR\%} = 0.0436\ \mathrm{QTAB}^{1.5} \qquad (3\text{-}5)$$

where

TITR% = the results from tests using the standard potentiometric titration procedure, and
QTAB = the corresponding readings obtained for the Quantab titrator strips.

Results of the regression analysis indicate that the estimated value for the slope, .0436, is significantly different from 0 at the 5-percent level of significance. The results of the analysis of variance indicate that the error sum of squares for the predicted values (error) is small compared to the error sum of squares for the regression.

The regression analysis indicates that a good relationship exists between the results from the standard potentiometric titration procedure and the results obtained from tests conducted with the Quantab titrator strips. A plot of the Quantab titrator strips number as a function of the potentiometric titration results and the 95-percent confidence limits for the predicted value are presented in Figure 3-4.

Comparison of the Test Methods

Following completion of the first series of tests, the selected methods were compared to determine which method was more suitable for determining the chloride content of concrete specimens in the field. These comparisons were based on the accuracy in predicting results obtained using the standard potentiometric titration procedure, the costs associated with the

Table 3-6. Comparison of the potentiometric titration and the Quantab titrator strip results for acid soluble chlorides at w/c = .47.

Specimen	Potentiometric Titration (%Cl)	Quantab Titrator Strip Reading
C-0	.023	.020
C-0	.018	.080
C-0	.020	1.20
C-0	.020	0.60
C-1	.026	0.70
C-1	.027	0.60
C-1	.027	0.80
C-1	.021	0.60
C-2	.032	0.80
C-2	.028	0.80
C-2	.032	0.60
C-2	.033	0.60
C-3	.049	1.80
C-3	.045	0.80
C-3	.049	0.85
C-3	.049	1.00
C-4	.064	0.50
C-4	.063	1.25
C-4	.062	1.10
C-4	.060	1.40
C-5	.111	2.15
C-5	.115	2.00
C-5	.115	2.05
C-5	.112	1.95
C-6	.198	2.60
C-6	.191	2.80
C-6	.189	3.20
C-6	.191	3.00
C-7	.222	3.10
C-7	.222	3.40
C-7	.221	2.95
C-7	.220	2.85
C-8	.330	4.20
C-8	.330	3.40
C-8	.329	2.95
C-8	.328	2.85
C-9	.388	4.30
C-9	.396	3.80
C-9	.386	4.35
C-9	.386	4.55

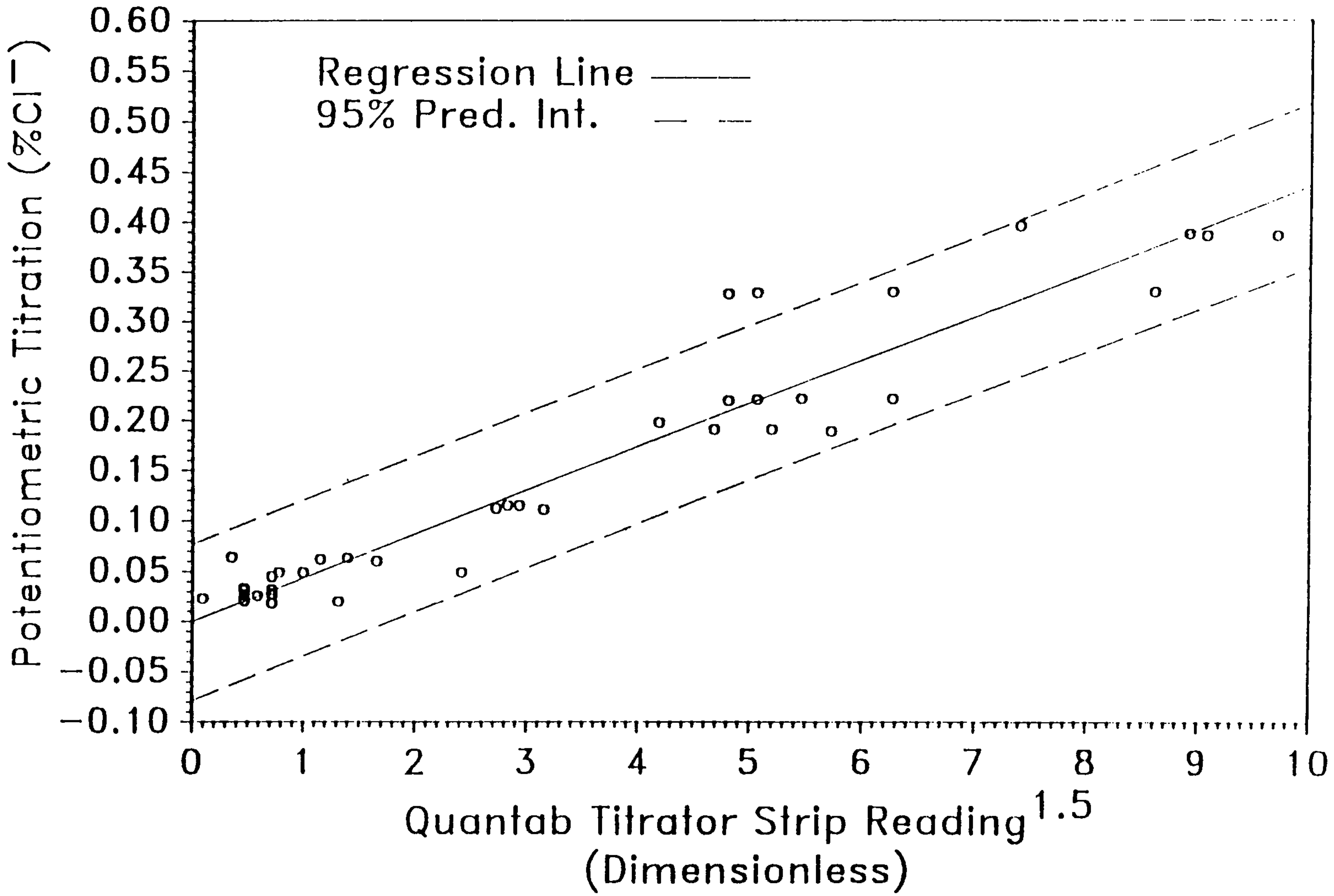


Figure 3-4. Potentiometric titration versus Quantab titrator strips.

purchase of the equipment and chemicals necessary for analysis, the speed or time required to weigh, prepare, and analyze individual samples, the level of expertise required in using the procedure without sacrificing accuracy, and the limitations associated with using the procedure in the field.

The standard potentiometric titration method was used to standardize the 0.01N silver nitrate and sodium chloride solutions used for the analysis of chloride in accordance with AASHTO T260-84. Tests for chloride content using the four selected methods were performed on standardized solutions to verify their accuracy prior to testing the specimens. The test results for all four selected methods were within the range of accuracy specified by the manufacturers.

As indicated from the analysis of the results obtained from the first series of tests for chloride, the highest accuracy is achieved using the specific ion probe, followed by the digital titrator, the spectrophotometer, and the Quantab titrator strips (Table 3-7). Accuracy is considered the most important criterion for selecting the appropriate method since it bears directly on the objective of the research--measuring the chloride content of bridges.

The initial cost of the specific ion probe was greater than the other selected methods. There are hidden costs associated with the spectrophotometer, the digital titrator, and the Quantab titrator strips. Items such as filter paper, beakers, stirring rods, nitric acid, and deionized water are required for all three methods. Additional items such as funnels, funneling apparatus, and pipets are required for the spectrophotometer and the digital titrator. Finally, a magnetic stirrer and magnetic stirring rods are desirable when using the digital titrator.

No special sample preparation is required for the specific ion probe. The probe can be calibrated in less than 10 minutes, after which samples can be weighed and analyzed in less than 10 minutes. The procedures for weighing and preparing the sample for the spectrophotometer and the digital titrator requires the same amount of time. After the samples are prepared, the analysis procedure using the spectrophotometer requires a little less time than the digital titrator. The operator must pay particular attention during the titration procedure when using the digital titrator so that the midpoint of the titration will be recognized. The procedure for weighing and preparing the sample to be analyzed using the Quantab titrator strips does not require as much time as for the spectrophotometer and the digital titrator. However, sometimes the operator may be required to wait as long as 20 minutes before the results can be read using the Quantab titrator strips.

Table 3-7. Comparison of test methods.

Method	Accuracy R-sq (Adjusted)	Cost[a]	Speed[b]	Level of Expertise[c]
Specific Ion Probe	99.0%	$1,860.90	1	Simple
Spectrophotometer	96.3%	$1,363.57	2	Medium
Digital Titrator	98.3%	$ 156.74	3	Medium
Quantab Titrator Strips	91.2%	$ 49.30	4	Simple

[a] Cost represents the initial cost of the equipment and the chemicals necessary for analyzing 40 specimens.
[b] Speed represents the order in which samples may be weighed, prepared, and tested using each method.
[c] Level of expertise gives an indication of how complicated each procedure is to use.

The analysis procedure for the specific ion probe was simplified for the operator, compared to the original procedure developed by James Instruments. Essentially, the operator records readings displayed by the electrometer while following a step-by-step procedure. Precautions must be followed in using this procedure, in order to obtain accurate results. Otherwise, the procedure is simple, quick, and straightforward. Procedures for the spectrophotometer and the digital titrator are a little more complicated than for the specific ion probe. The operator not only needs to realize the importance of following the procedure completely, but also must be able to detect interferences that may occur and compensate for them. The analysis procedure for using the Quantab titrator strip is a little more complicated than the procedure for the specific ion probe, but requires little technical expertise.

By considering each of the criteria for selecting the method for determining the chloride content of concrete, summarized in Table 3-7, the specific ion probe was determined to be most suitable for the purpose intended. First of all, the apparatus required for the spectrophotometer and the digital titrator are more suited for use in the laboratory than in the field. Second, both of these procedures require a certain level of expertise to achieve meaningful results. Finally, the Quantab titrator strips do not provide the accuracy that is desirable for determining the time to depassivation and, at times, may require an excessive amount of time for analysis. Therefore, the specific ion probe was investigated further to study the effects of cement contents and reaction temperature.

Effects of Cement Content on the Selected Method

The specific ion probe was tested to determine the effects that differences in cement content representative of substructure and superstructure concrete have on measuring the chloride content. For this series of tests, the potentiometric titration procedure was used as the control method in determining the chloride content of the test specimens. However, the powdered concrete samples were screened, and the material larger than No. 50 mesh was discarded prior to chloride content analysis.

The specific ion probe was subjected to testing concrete with water-to-cement ratios of .40 and .50 at various chloride contamination levels. Chloride contaminations levels of 0.2, 0.8, 1.6, 3.2, 6.4, 8.6, 10.8, and 12.8 lb Cl/yd^3 (0.1, 0.5, 1.0, 1.9, 3.8, 5.1, 6.4, and 7.6 kg/m^3) of concrete were used for the specimens with a w/c equal to .40. Specimens with a w/c equal to .50 were tested at similar chloride contamination levels, with one exception. One specimen containing no added chloride was tested in place for the 0.2 lb Cl/yd^3 (0.1 kg/m^3) contamination level. The results of the specific ion probe test and the standard test method are presented in Table 3-8.

The millivolt readings for the specific ion probe, presented in Table 3-8, were converted to percent of chloride using the procedure presented in the first series of tests for chloride content determination. After the values for percent Cl as measured with the specific ion probe were determined, the results presented in Table 3-8 were compared with the results from the first series of tests (Table 3-3). Graphical results of this comparison are presented in Figure 3-5, which shows that there appears to be no significant effect of cement content on the performance of the specific ion probe. The results obtained for specimens having water-to-cement ratios of .40 and .50, when compared to the results from the first series of tests, do not show specific trends.

A regression analysis was performed to determine the relationship between the results from the standard potentiometric titration procedure and the specific ion probe presented in Tables 3-3 and 3-8. Weak correlations between cement content and potentiometric titration results were noted during the analysis confirming earlier suspicions that the results from the specific ion probe were not significantly affected by differences in cement content. The most appropriate regression equation using the specific ion probe for the data presented in Tables 3-3 and 3-8 is as follows:

$$\text{TITR\%} = 0.500\ \text{\%JAMES}^{0.8} \tag{3-6}$$

Table 3-8. Potentiometric titration and specific ion probe results for different cement contents.

Specimen	w/c	Potentiometric Titration (%Cl)	Millivolt Reading	Specific Ion Probe Calculated %Cl
DC-1	.40	.021	76.8	.015
	.40	.020	76.6	.015
DC-3	.40	.037	53.7	.041
	.40	.039	52.5	.043
DC-4	.40	.064	35.6	.088
	.40	.064	37.2	.083
DC-5	.40	.083	27	.127
	.40	.091	25.6	.135
DC-6	.40	.158	9	.275
	.40	.154	6.1	.312
DC-7	.40	.184	1.9	.373
	.40	.188	.4	.398
DC-8	.40	.270	-3.2	.442
	.40	.264	-2.7	.433
DC-9	.40	.315	-9.2	.572
	.40	.315	-7.1	.522
EC-0	.50	.018	90	.008
	.50	.020	90.8	.008
EC-3	.50	.037	52.5	.039
	.50	.036	53.5	.038
EC-4	.50	.057	36.5	.078
	.50	.059	35.4	.081
EC-5	.50	.101	23.4	.135
	.50	.103	24	.132
EC-6	.50	.187	2.4	.329
	.50	.185	5.9	.284
EC-7	.50	.224	-2.9	.400
	.50	.230	-1.3	.374
EC-8	.50	.313	-7.5	.486
	.50	.312	-10.9	.562
EC-9	.50	.380	-13.4	.625
	.50	.384	-14.2	.646

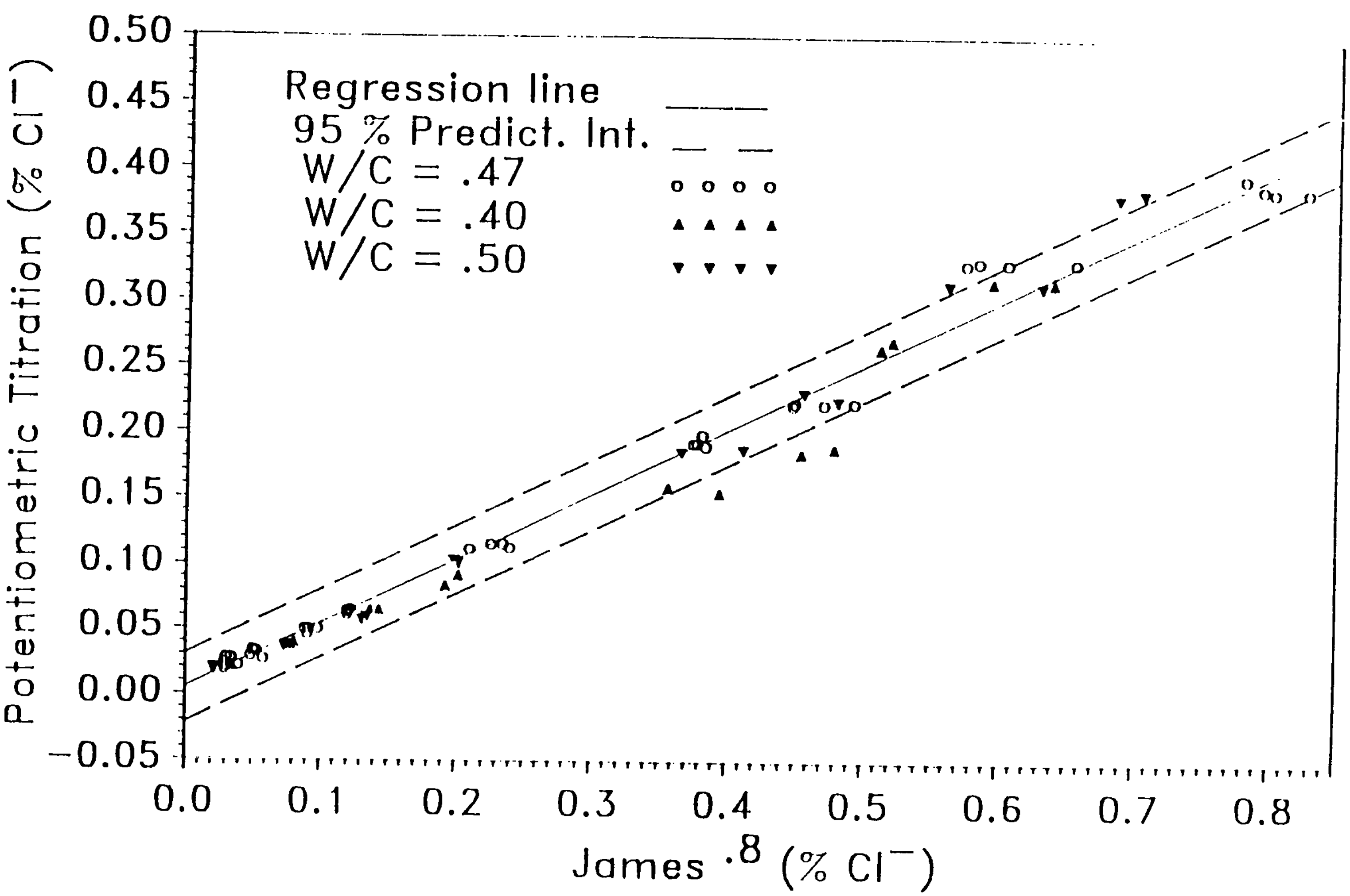


Figure 3-5. Potentiometric titration versus the specific ion probe for effects of cement content.

where

TITR% = the results from tests using the standard potentiometric titration procedure, and
%JAMES = the corresponding results for %Cl obtained using the specific ion probe.

Results of the regression analysis indicate that the estimated value for the slope is significantly different from 0 at the 5-percent level of significance. The coefficient of determination, R^2, is irrelevant in the regression analysis since the value for the intercept was previously determined to be equal to zero. The results of the analysis of variance indicate the error sum of squares for the predicted values (error) is very small compared to the error sum of squares for the regression. In summary, the results indicate that a strong relationship exists between the results obtained using the specific probe and the standard potentiometric titration procedure as evidenced by an F value of 10139.63.

Effects of Temperature on the Selected Method

The specific ion probe was also subjected to testing concrete at a single chloride contamination level to determine the effects of temperature in measuring the chloride content. Concrete representative of bridge decks (w/c = .47) and having a chloride content of 1.6 lb/yd^3 (1.0 kg/m^3) was selected for this series of tests. The physical characteristics of the concrete (Batch C-4), are presented in Table 3-1.

Samples were tested at temperatures ranging from 34 to 130°F (1 to 54°C) using the procedure for the specific ion probe. The results are shown in Table 3-9. The millivolt readings for the specific ion probe are also presented in percent of chloride in Table 3-9, using the calibration procedure employed in the first series of tests for chloride content determination. After the values for percent Cl as measured with the specific ion probe were determined, the results were compared with those for specimen C-4 from the first series of tests (Table 3-3) to determine the effects of temperature.

Table 3-9. Specific ion probe test results for the effect of reaction temperature.

Specific	Test Temperature (°F)	Specific Ion Probe Millivolt Reading	Specific Ion Probe Calculated (%Cl)	Reaction Temperature (°F)
C-4	34	30.7	.099	49
C-4	34	32.4	.092	37
C-4	34	34.6	.084	42
C-4	34	29.3	.105	39
C-4	40	32.5	.095	46
C-4	40	31.4	.100	44
C-4	50	29.0	.101	58
C-4	50	33.5	.083	58
C-4	50	32.8	.086	54
C-4	50	31.4	.100	57
C-4	50	35.6	.084	56
C-4	50	35.0	.086	59
C-4	50	38.5	.074	58
C-4	70	43.7	.059	77
C-4	70	42.2	.063	79
C-4	70	35.6	.084	79
C-4	70	43.5	.060	79
C-4	70	45.3	.055	83
C-4	70	44.9	.056	75
C-4	70	39.8	.069	80
C-4	70	40.9	.066	77
C-4	90	43.2	.060	92
C-4	90	41.1	.066	94
C-4	90	40.9	.066	94
C-4	90	42.7	.061	92
C-4	110	48.6	.047	113
C-4	100	48.8	.047	114
C-4	110	45.8	.054	114
C-4	110	47.3	.050	112
C-4	130	57.4	.033	123
C-4	130	53.8	.039	127
C-4	130	53.8	.039	127
C-4	130	51.5	.043	132

A regression analysis was performed to determine the relationship between changes in the reaction temperature and the results from the specific ion probe. The regression equation for the effects of temperature using the specific ion probe is as follows:

$$\text{ACTUAL - \%JAMES} = -0.103 + 0.0119\ \text{REACTTEMP}^{.5} \qquad (3\text{-}7)$$

where

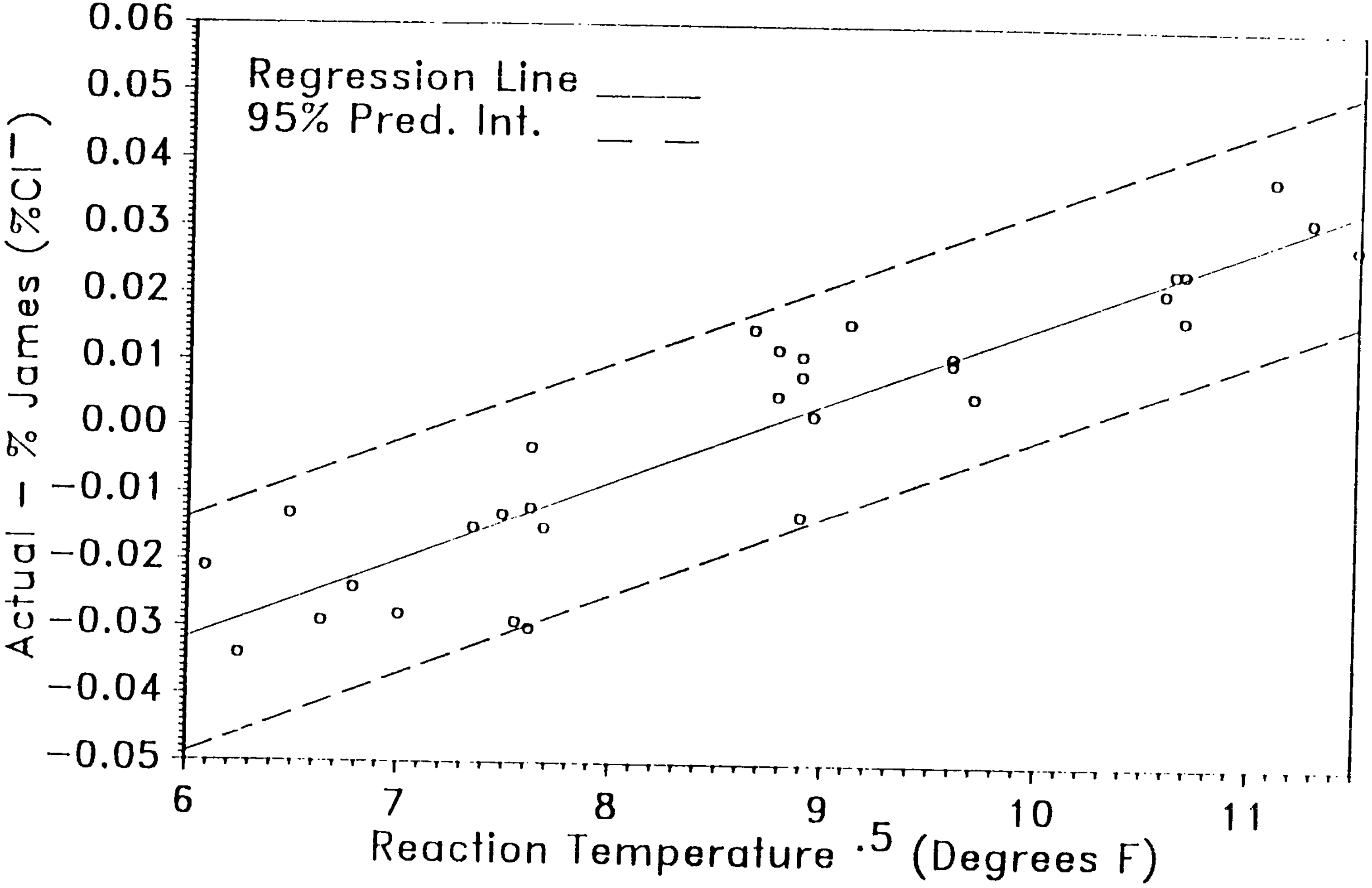
ACTUAL - %JAMES = the difference in the results from tests using the specific ion probe during the first series of tests as presented in Table 3-3 and the corresponding results presented in Table 3-9, and

REACTTEMP = the various temperatures of the reaction resulting from the test procedure, as presented in Table 3-9.

Results of the regression analysis indicate that the estimated value for the slope is significantly different from 0 at the 5-percent level of significance, while the intercept is not. The coefficient of determination, R^2, indicates that 84.7 percent of the variation in the difference in the results from the first series of tests and the results presented in Table 3-9 can be predicted from the independent variable REACTTEMP (the reaction temperature for the specific ion probe). The results of the analysis of variance indicate the error sum of squares for the predicted values (error) is small compared to the error sum of squares for the regression.

The results of the regression analysis support the determined relationship of the effects of temperature for the specific ion probe. Though not strong when compared to results from previous analyses, the relationship does exist and, among other parameters, is evidenced by an F value of 171.01. Figure 3-6 illustrates the relationship between the correction factor for the specific ion probe suggested by the results of the regression analysis and the reaction temperature.

In order to further evaluate the effects of temperature, additional studies were carried out using pure saline solutions at chloride concentrations of 0.0249, 0.2493, and 1.2465 percent (equivalent to 1, 10, and 50 lb/yd^3 [0.6, 6.0, and 29.8 kg/m^3]) in lieu of solutions extracted from concrete. The purpose of using pure saline solutions was to eliminate possible interferences from extraneous ions. Two containers of each concentration level were suspended in 2 in. (5 cm) of water by a styrofoam collar. The temperature of the water was initially decreased to 40°F (4.4°C) by the addition of ice into the water bath. The ice water was replaced with either cold or hot water to gradually achieve 10°F (5.6°C) increments to a final temperature of 120°F (48.9°C).



Note: °C = (°F-32) 5/9

Figure 3-6. Temperature correction for the specific ion probe.

The effect of temperature on the pure chloride concentration was investigated using two fixed probe-meter combinations (FPMC A and FPMC B). Two millivolt readings were recorded for each temperature level for each of the three chloride concentration levels. The predicted chloride concentrations were calculated for each millivolt reading, as shown in Table 3-10. For millivolt to percent chloride conversion, the triple set of calibration solutions was used with the following results:

Predictor	Coefficient	Standard Deviation	t-Ratio	P
Constant	-0.41450	0.001810	-22.90	0.028
mV -0.0179332	0.0002693	-66.59	0.010	

$s = 0.02123$
R^2 (adj) $= 100.0\%$

$$\text{LOG } Y = -0041450 - 0.0179332 \text{ mV} \qquad (3\text{-}8)$$

The statistical analysis of the parameters of the equation produced the following:

Hypothesis: $\alpha = 0 \quad t_{crit} = \underline{+}12.706$
Alternative: $\alpha \neq 0 \quad t_{calc} = -22.90$

Hypothesis: $\beta = 0 \quad t_{crit} = 12.706$
Alternative: $\beta \neq 0 \quad t_{calc} = -66.59$

The results indicate that as temperature increases, the millivolt readings increase.

The difference between the predicted and actual percent chloride and temperature relation was investigated statistically to determine the significance of each slope at different chloride concentrations:

Table 3-10. Effects of temperature on the percent chloride prediction.

Concentration: 0.0249% Chloride

	Reading No. 1		Reading No. 2	
Temperature (°F)	Millivolt Reading	%Cl	Millivolt Reading	%Cl
FPMC A				
50	59.4	0.0315	64.10	.0258
60	60.9	0.0295	64.70	.0251
70	63.2	0.0268	67.60	.0222
80	66.0	0.0238	69.90	.0201
90	65.7	0.0241	69.60	.0205
100	76.2	0.0157	78.10	.0145
120	80.2	0.0133	80.70	.0130
FPMC B				
50	32.2	0.0594	35.90	.0501
60	38.5	0.0445	42.50	.0370
70	45.2	0.0327	49.60	.0267
80	49.7	0.0266	53.30	.0225
90	66.2	0.0159	70.60	.0131
100	67.4	0.0151	71.10	.0128
120	75.5	0.0106	79.20	.0090

Concentration: 0.2493% Chloride

	Reading No. 1		Reading No. 2	
Temperature (°F)	Millivolt Reading	%Cl	Millivolt Reading	%Cl
FPMC A				
50	5.9	0.3064	3.20	.3437
60	7.1	0.2912	6.90	.2936
70	8.1	0.2790	7.80	.2826
80	9.3	0.2652	8.50	.2743
90	10.1	0.2386	10.40	.2357
100	13.3	0.2091	14.00	.2032
120	16.6	0.1825	16.30	.1848
FPMC B				
50	-8.8	0.3912	-9.20	.3985
60	-7.5	0.3685	-7.40	.3668
70	-4.9	0.3270	-4.40	.3196
80	-3.1	0.3010	-3.00	.2997
90	4.4	0.2331	5.20	.2251
100	6.5	0.2127	6.90	.2091
120	9.8	0.1843	11.10	.1742

Table 3-10. *(continued).*

Concentration: 1.2465% Chloride

	Reading No. 1		Reading No. 2	
Temperature (°F)	Millivolt Reading	%Cl	Millivolt Reading	%Cl
FPMC A				
50	-37.3	0.0315	-37.4	0.0258
60	-37.1	0.0295	-37.1	0.0251
70	-35.5	0.0268	-35.6	0.0222
80	-35.8	0.0238	-36.1	0.0201
90	-33.4	0.0241	-34.7	0.0205
100	-32.6	0.0157	-33.1	0.0145
120	-31.0	0.0133	-31.6	0.0130
FPMC B				
50	-43.7	0.0594	-41.6	0.0501
60	-43.5	0.0445	-43.0	0.0307
70	-43.1	0.0327	-42.7	0.0267
80	-43.8	0.0266	-43.5	0.0225
90	-40.0	0.0159	-39.9	0.0131
100	-39.3	0.0151	-39.4	0.0128
120	-40.1	0.0106	-37.4	0.0090

Concentration Level 0.0249

Predictor	Coefficient	Standard Deviation	t-Ratio	P
Constant	0.016389	0.002590	6.33	0.000
Temp -0.000238	0.0000307	-7.76		0.000

s = 0.002561
R^2 (adj) = 82.0%

Concentration Level 0.2493

Predictor	Coefficient	Standard Deviation	t-Ratio	P
Constant	0.17330	0.01138	15.22	0.000
Temp -0.0020414	0.0001348	-15.14	0.000	

s = 0.01126
R^2 (adj) = 94.6%

Concentration Level 1.2465

Predictor	Coefficient	Standard Deviation	t-Ratio	P
Constant	1.23516	0.08576	14.40	0.000
Temp -0.010078	0.001016	-9.92		0.000

s = 0.08481
R^2 (adj) = 88.2%

A t-test was used to compare the slopes. Using the 0.0249 concentration as a base, the hypothesis and t results are shown below:

Hypothesis: $\alpha = -0.002054$ $t_{crit} = \pm 2.571$
Alternative: $\alpha \neq -0.002054$ $t_{calc} = 4.1575$

Hypothesis: $\alpha = -0.010078$ $t_{crit} = \pm 2.571$
Alternative: $\alpha \neq -0.010078$ $t_{calc} = 22.6848$

The results of the test concluded that significant differences exist between slopes at the different concentrations. This result implies that each concentration level reacts differently to temperature. Therefore, a uniform temperature correction equation is an invalid correction method.

4

Field Validation of the Selected Method

Site Selection

For field validation, 13 bridges were selected for testing from four different environmental exposure groups. The different environmental exposure groups were defined according to the soil freezing index. The soil freezing index combines elements of time and temperature into one component of measure in terms of degree days. One degree day is defined as one day having a mean air temperature corresponding to 1°F (0.6°C) below freezing, or 31°F (-0.6°C) (*27*). The soil freezing index was considered appropriate for defining different environmental exposure groups relative to the amount of salt being applied on bridges.

Florida was selected to represent the coastal region with 0 freezing-degree days per year. A non-coastal area of Virginia was selected, having 0 freezing-degree per days per year according to the index. The third environmental exposure group, Pennsylvania, has 0 to 500 freezing-degree days per year, and Wisconsin was designated to represent the fourth environmental exposure group having 1,000-plus freezing-degree days per year (*27*).

After the bridges were selected for field validation of the ion probe, the following tests were done:

- Modifications of the procedure for the specific ion probe,
- Development of the sampling procedure,

- Determination of the most viable method of weighing samples,
- Determination of whether samples needed to be crushed prior to analysis, and
- Development of the final procedure for validating the accuracy of the results for the specific ion probe.

Sample Collection Equipment and Procedure

Obtaining a representative sample of the material to be analyzed is considered as important as the accuracy of the method used for analyzing concrete samples for chloride. The standard procedure for sampling in accordance with AASHTO T260-84 (*23*) provides that the drill bit used for the pulverizing method of sampling be of sufficient diameter to allow a representative sample. The hole is drilled with a rotary hammer to within 1/2 in. (13 mm) of the desired drilling depth by setting the depth indicator on the drill. Next, the hole is cleaned thoroughly using a blow out bulb. The depth indicator is again reset for an additional 1/2-in. (13-mm) drilling to collect the sample. For this portion of the drilling operation, some users elect to use a bit that is 1/4 in. (6 mm) smaller in diameter to prevent contamination from the sides of the drill hole. Ten grams of sample are collected from the powdered concrete remaining in the drill hole using a spoon, and the sample is placed in a sample container. Prior to testing, the sample is crushed until the entire sample passes through a No. 50 sieve.

In developing the sampling procedure for testing the 13 bridges, researchers considered the size distribution of the coarse aggregate as the primary factor influencing the test results for chloride. The sampling procedure selected for field use consisted of drilling holes using a rotary impact drill and a 1 1/8-in. (29-mm) -diameter Heller bit. This diameter was considered sufficiently large to negate or minimize the influences that the coarse aggregate (3/4-in. (19 mm) maximum size) may have on the test results. Centering the drill hole over a large aggregate particle was not considered likely. The Heller bit is designed to allow drill cuttings to be removed from the drilling surface by means of a vacuum system. A drillstop with 1/4-in. (6-mm) division marks controls the drilling depth. A sampling collection unit was designed to decrease the time required to collect samples when compared to the standard procedure described in AASHTO T260-84 (*23*). The sample collection system consists of a 2.25 hp wet and dry vacuum cleaner fitted with a plexiglass sample collection chamber, coffee filters, and plastic tubing connected to the Heller bit assembly. The system significantly reduces the concrete sample collection time. Figure 4-1 shows the sample extraction and collection system in operation. Removal of the collected sample on the filter is shown in Figure 4-2.

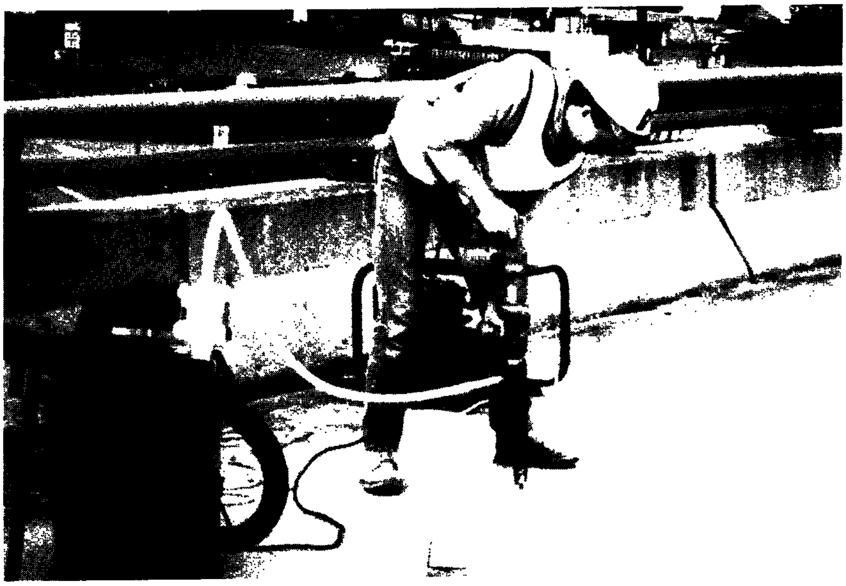


Figure 4-1. Sample extraction and collection system in operation.

Figure 4-2. Sample collected on filter removed from collection chamber.

Other equipment included a single phase generator and pachometer. The generator was used to supply electricity for the rotary impact drill and the sample collection unit. A pachometer is a magnetic flux device that is used for determining the position of the reinforcing steel in the concrete.

Calibration of the Specific Ion Probe

During the laboratory investigation of the specific ion probe, certain trends were noticed in the readings obtained when measuring concrete specimens for chloride content. In addition, James Instruments, Inc. (communication with James Instruments, Inc., 1989) was contacted regarding factors that may reduce the accuracy in the results obtained when using the specific ion probe. Subsequently, the procedure for measuring the chloride content was modified.

Modifications of the procedure for measuring the chloride content in concrete with the specific ion probe required interpretation of the trends in the readings on the electrometer during the course of an observation. Three minutes after waiting for the reading on the specific ion probe to stabilize, subsequent changes in the electrometer are recorded. Three examples are presented below:

Example 1	Example 2	Example 3
88.3	88.3	88.3
88.1	88.1	88.2
88.0	88.0	88.1
87.9	88.1	88.0
88.0	88.0	87.9
87.9	88.0	88.0
88.0	87.9	87.9

In the examples presented, the appropriate reading on the electrometer to record is 88.0 mV. However, any reading within 0.1 or 0.2 mV of this number will not reduce the accuracy of the final results significantly. The actual trends observed during use may not be exact but should be similar. Abnormal errors in the results using the specific ion probe may occur if certain precautions are not observed. Precautions recommended by James Instruments, Inc. to prevent the occurrence of this type of error are presented in Appendix A.

The procedure for testing concrete specimens using the specific ion probe was modified prior to the field investigation in an attempt to improve the accuracy and the repeatability of the measurements and to minimize errors associated with different operators.

The specific ion probe is calibrated against a set of three standard liquids containing 0.005-, 0.05-, and 0.50- percent chloride each time it is used. The probe is filled with a solution containing a wetting agent until the level reaches the filling hole. The voltmeter is turned on, and the probe is placed in each liquid for approximately 3 minutes or until the reading does not change more than 0.2 mV during a 60-s period. The probe is rinsed with distilled water after each test. The following experimental procedure was used to determine the variability between each batch of tests and within each set of tests:

1. Powdered samples were taken from seven concrete specimens cast in the laboratory containing 0.0-, 0.4-, 1.6-, 3.2-, 6.4-, 10.8-, and 12.8- percent chloride. Using a masonry bit 3/4 in. (19 mm) in diameter, 2-in. (5-cm) holes were drilled vertically into the concrete specimens. The material passing a No. 50 (300 μm) sieve was placed into beakers and oven dried.

2. The voltmeter was turned on and the specific ion probe was calibrated using three sets of three standard liquids containing 0.005-, 0.05-, and 0.5- percent chloride.

3. Two 3.0-g samples were tested from each specimen using the modified specific ion probe method described in Appendix A.

4. The voltmeter was turned off after all specimens were tested; steps 2 and 3 were repeated four times.

The log (base 10) of the standard liquids (dependent variable) was regressed against the reading from the probe (independent variable). One regression equation was produced for each set of standard liquids. The general form of the resultant regression is as follows:

$$(\%Cl) = 10^{[a+b\,(mV)]} \tag{4-1}$$

where

a and b = regression coefficients,
mV = electrometer reading with the probe placed in the standard chloride solution, and
%Cl = chloride content of the standard chloride solution.

The relationship between the potentiometric titration values (percent chloride) and the specific ion probe results to the 0.8th power (percent chloride$^{0.8}$) is shown in Figure 4-3. The majority of the results fall inside the 95-percent prediction interval, indicating that the results are consistent and repeatable at the 2.5-percent level of significance.

To examine the variance among results from three sets of standard liquids and the variance among four calibration runs, a two-way analysis of variance test was performed. The results are presented in Table 4-1. The total variation is partitioned into four sources: variation due to sets; variation due to calibration runs; variation due to interaction between sets and runs; and variation due to error.

Three tests based on mean squares (MS) results were performed to measure the strength of the relationship. The first test examined the interaction between the sets and the calibration runs; the second test examined the effect of the sets; and the third test examined the effect of the calibration runs. Tests 1 through 3 indicated no interaction between sets and batches or within the sets or batches. Thus, the sets of standard liquids and the calibration runs are independent.

The two-way analysis of variance tests illustrate that the specific ion probe produces consistent results with a very small variance, independent of the number of samples per specimen and the calibration run. The majority of the variance is due to the specific ion probe, as shown by the magnitude of the sum of squares value for the error term. Although no reaction temperatures were recorded, it is suspected that the major portion of the variance is associated with varying reaction temperatures. The calibration procedure provided by James Instrument Company uses an upper chloride concentration of 0.5 percent. Therefore, it is inadvisable to extrapolate potentiometric titration values for specific ion probe readings beyond this limit unless the calibration range is expanded.

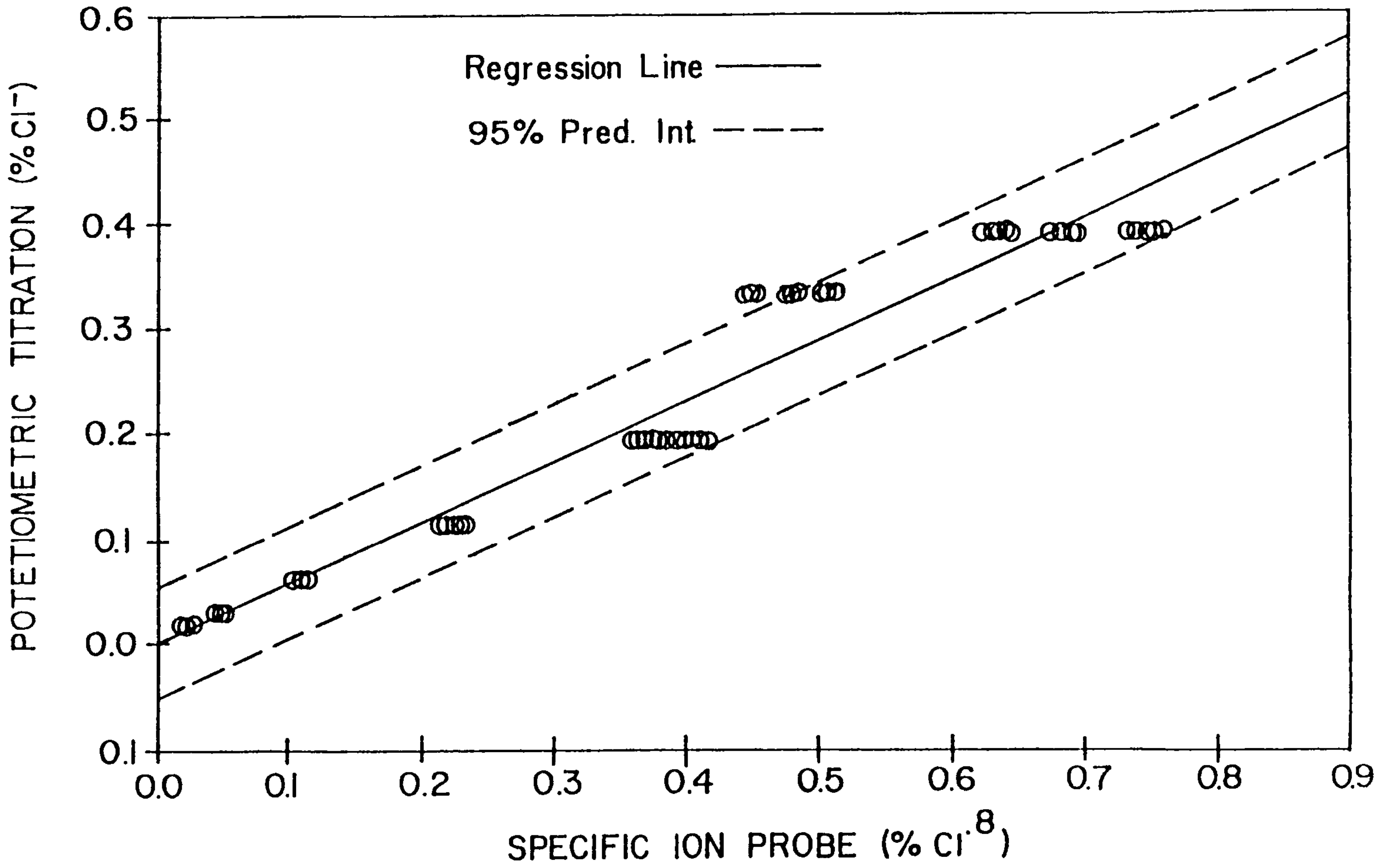


Figure 4-3. Potentiometric titration versus specific ion probe for all data.

Table 4-1. Output from two-way analysis of variance for the specific ion probe (percent chloride).

Source	Degrees of Freedom	Sum of Squares	Mean Squares
Set	2	0.0302	0.0151
Run	3	0.0017	0.0006
Interaction	6	0.0003	0.0001
Error	156	7.7357	0.0496
Total Variation	167	7.7679	

Analysis of Weighing Methods

The specific ion probe method requires a 3.0-g sample. In the original James Instruments procedure *(20)*, a 3.0-g sample is measured using two quantities of a 1.5-g capacity plastic vial. The accuracies of a field balance and a triple beam balance were investigated to streamline the procedure for sample quantification. Samples were prepared and re-weighed on a Mettler H31 AR Precision Scale to the nearest 0.0001 g. The AASHTO Test T260-84 requires the concrete powder to pass a No. 50 (300 μm) sieve. Therefore, only materials passing this sieve were used in weighing accuracy analysis. The following cases were adopted:

Case 1: The accuracy of a single 1.5-g plastic vial. A sample of concrete powder is firmly compacted to a premeasured red line using the flat end of a pen. Seventy measurements were recorded.

Case 2: The accuracy of a set of 20 plastic vials, each vial prepared using the method described in Case 1.

Case 3: The accuracy of a set of 35 3.0-g samples consisting of paired samples from Case 1.

Case 4: The accuracy of 30 3.0-g samples weighed on a James Instruments, Inc. field balance.

Case 5: The accuracy of 30 3.0-g samples weighed on an Ohaus 800 Series Triple Beam Balance.

Normal probability plots were generated and used to ensure that a sufficient number of samples were prepared and that these represented a random sample from a normal distribution. The results indicate that it is reasonable to assume that the data were originated from a normal population.

The t-distribution was used to calculate the 95-percent confidence interval since the true standard deviation of the population was not known. This assumption is valid since the t-distribution approximates the normal distribution for 30 samples or more. The 95-percent confidence interval indicates the range of values that the instrument is capable of weighing with this level of accuracy. A smaller interval would connote a more precise value of the mean weight.

The t-test was used to find the mean weight of the concrete powder using different instruments. For the first trial, the expected weight was used in the formulation of the null hypothesis. In all cases, this resulted in very small p-values, indicating that the mean is not close to the expected weight. Using values closer to the sample mean for the second trial resulted in the majority of p-values being close to 1.0, indicating that the sample mean is more representative than the expected weight. The results of various weighing methods are presented in Table 4-2. In summary, the accuracy in the James procedure (vials) was determined to be 3.04 ± .05 g. Using this procedure in the field was determined to be very time-consuming. The time required to weigh the samples in the field ranged from 5 to 6 minutes. The balance supplied by James Instruments, Inc. did not maintain sufficient accuracy for weighing the concrete specimens. However, the accuracy for a triple beam balance, 3.04 ± .05 g, was considered acceptable. Consequently, the triple beam balance is recommended. It requires a weighing time of 1 1/2 to 2 minutes for each specimen.

Table 4-2. Results of various weighing methods.

Case	Number of Measurements	Mean	Standard Deviation	95-Percent Confidence Interval
1. 1.5g vial	70	1.52	0.056	1.51 - 1.54
2. Set of vials	40	1.48	0.042	1.47 - 1.49
3. 2 x 1.5g vials	35	3.04	0.090	3.01 - 3.07
4. Field Balance	30	2.06	0.110	3.02 - 3.10
5. Triple Beam Balance	30	3.04	0.050	3.03 - 3.06

Note: The 95-percent confidence interval is calculated assuming a t-distribution.

Crushed Versus Uncrushed Sample

The first 20 samples collected from a bridge in Pennsylvania were tested using the specific ion probe to compare the test results for chloride from samples that were crushed to pass a No. 50 (300 μm) sieve with samples that were not crushed prior to testing for chloride. The initial results indicated a good relationship between the test results. Therefore, the remaining specimens were not crushed in the field prior to testing for chloride. Subsequently, 20 samples from one bridge in each of the four states were tested prior to crushing and after crushing to verify the relationship between crushing and not crushing the concrete powdered samples. The results of the tests for chloride on 80 samples from bridges in Pennsylvania, Virginia, Florida, and Wisconsin are presented in Table 4-3. This table presents the test results using the standard potentiometric titration procedure and the results for the specific ion probe on specimens that were not crushed and on specimens crushed to pass a No. 50 (300 μm) sieve.

The results presented in Table 4-3 were analyzed to determine the relationships between the samples that were crushed versus samples obtained prior to crushing using regression analysis. The regression analysis equation for the relationship between samples that were crushed and uncrushed prior to being subjected to chloride content determination using the specific ion probe is as follows:

Table 4-3. Field validation test results.

		Potentiometric Titration		Specific Ion Probe Test Results	
State	Bridge	Sample Number	Results (%Cl)	Crushed (%Cl)	Uncrushed (%Cl)
PA	11-15/35 NB	B-1	.076	.088	.099
		2	.027	.038	.035
		3	.014	.023	.016
		4	.018	.021	.013
		G-1	.047	.055	.073
		2	.019	.025	.016
		3	.018	.025	.021
		H-3	.027	.037	.036
		I-1	.111	.164	.192
		2	.025	.043	.032
		P1-2	.280	.384	.505
		3	.081	.138	.125
		4	.019	.030	.016
		5	.014	.023	.014
		P2-2	.032	.047	.042
		3	.013	.025	.017
		4	.015	.024	.014
		C1-4	.015	.022	.016
		C2-3	.025	.034	.032
		4	.015	.025	.017
VA	I81/927 NB	A-1	.256	.314	.397
		2	.096	.149	.173
		3	.030	.050	.038
		4	.020	.023	.021
		B-1	.389	.460	.850
		2	.183	.419	.367
		3	.216	.322	.353
		D-1	.380	.641	.855
		3	.142	.288	.299
		4	.101	.181	.207
		5	.074	.123	.123

Table 4-3. *(continued)*

State	Bridge	Potentiometric Titration Sample Number	Potentiometric Titration Results (%Cl)	Specific Ion Probe Test Results Crushed (%Cl)	Specific Ion Probe Test Results Uncrushed (%Cl)
		I-1	.220	.274	.378
		2	.124	.188	.226
		3	.051	.088	.081
		4	.021	.037	.033
		K-2	.107	.150	.152
		4	.025	.031	.025
		L-1	.258	.327	.525
		2	.142	.205	.263
		4	.039	.074	.056
FL	Rt. 312	F1-6	.106	.144	.172
		F2-2	.503	.750	.849
		3	.333	.600	.502
		4	.206	.403	.486
		5	.231	.428	.399
		6	.144	.242	.212
		P1-1	.338	.363	.509
		2	.260	.406	.341
		3	.170	.250	.228
		4	.120	.174	.167
		5	.073	.101	.103
		6	.026	.038	.031
		P2-1	.146	.180	.245
		2	.120	.151	.164
		3	.097	.129	.130
		4	.053	.074	.081
		5	.025	.042	.044
		6	.018	.026	.020
		P3-4	.013	.022	.015
		5	.011	.019	.013

Table 4-3. (*continued*)

		Potentiometric Titration		Specific Ion Probe Test Results	
State	Bridge	Sample Number	Results (%Cl)	Crushed (%Cl)	Uncrushed (%Cl)
WI	Rt. 252 WB	B-2	.453	.527	.717
		4	.220	.285	.294
		5	.132	.180	.167
		C-1	.319	.550	.591
		3	.265	.348	.341
		4	.148	.252	.264
		D-2	.344	.549	.757
		3	.365	.512	.605
		4	.220	.382	.381
		5	.138	.228	.223
		6	.054	.072	.067
		K-4	.144	.202	.184
		5	.101	.125	.117
		6	.040	.057	.045
		L-5	.155	.193	.219
		6	.077	.089	.086
		BW1-1	.605	.778	1.051
		3	.134	.208	.297
		4	.213	.282	.417
		5	.202	.275	.390

$$1/\mathrm{CRUSH} = -0.723 + 1.96\,(1/\mathrm{NOTCR}^{0.75}) \tag{4-2}$$

where

CRUSH = the results of the analysis for percent Cl using the specific ion probe on samples presented in Table 4-3 that have been crushed to pass a No. 50 (300 μm) sieve, and

NOTCR = the results of the analysis for percent Cl using the specific ion probe on samples presented in Table 4-3 that have not been crushed.

Results of the regression analysis indicate that the estimated value for the slope is significantly different from 0 at the 5-percent level of significance. The coefficient of determination, R^2, indicates that 97.7 percent of the variation in the dependent variable, the inverse of the results for the samples that were crushed, can be predicted from the independent variable, representing the results obtained from samples prior to crushing. The results of the analysis of variance indicate that the error sum of squares for the predicted values is very small in relation to the error sum of squares for the regression.

The regression analysis indicates that a strong relationship exists between the results for the samples that were tested with the specific ion probe prior to crushing and the results obtained after crushing the samples to pass a No. 50 (300 μm) sieve. A plot of the results obtained using the specific ion probe illustrating the relationship between crushed and uncrushed samples and the 95-percent confidence limits for the prediction interval is presented in Figure 4-4.

The regression equation for the relationship between the results from the potentiometric titration procedure and the specific ion probe for samples that were not crushed is:

$$\mathrm{TITR\%} = -0.00895 + 0.513\,(\mathrm{NOTCR}^{0.8}) \tag{4-3}$$

where

TITR% = the results of the analysis for percent chloride using potentiometric titration on samples in Table 4-3 that were not crushed, and

NOTCR = the results of the analysis for percent chloride using the specific ion probe on samples in Table 4-3 that were not crushed.

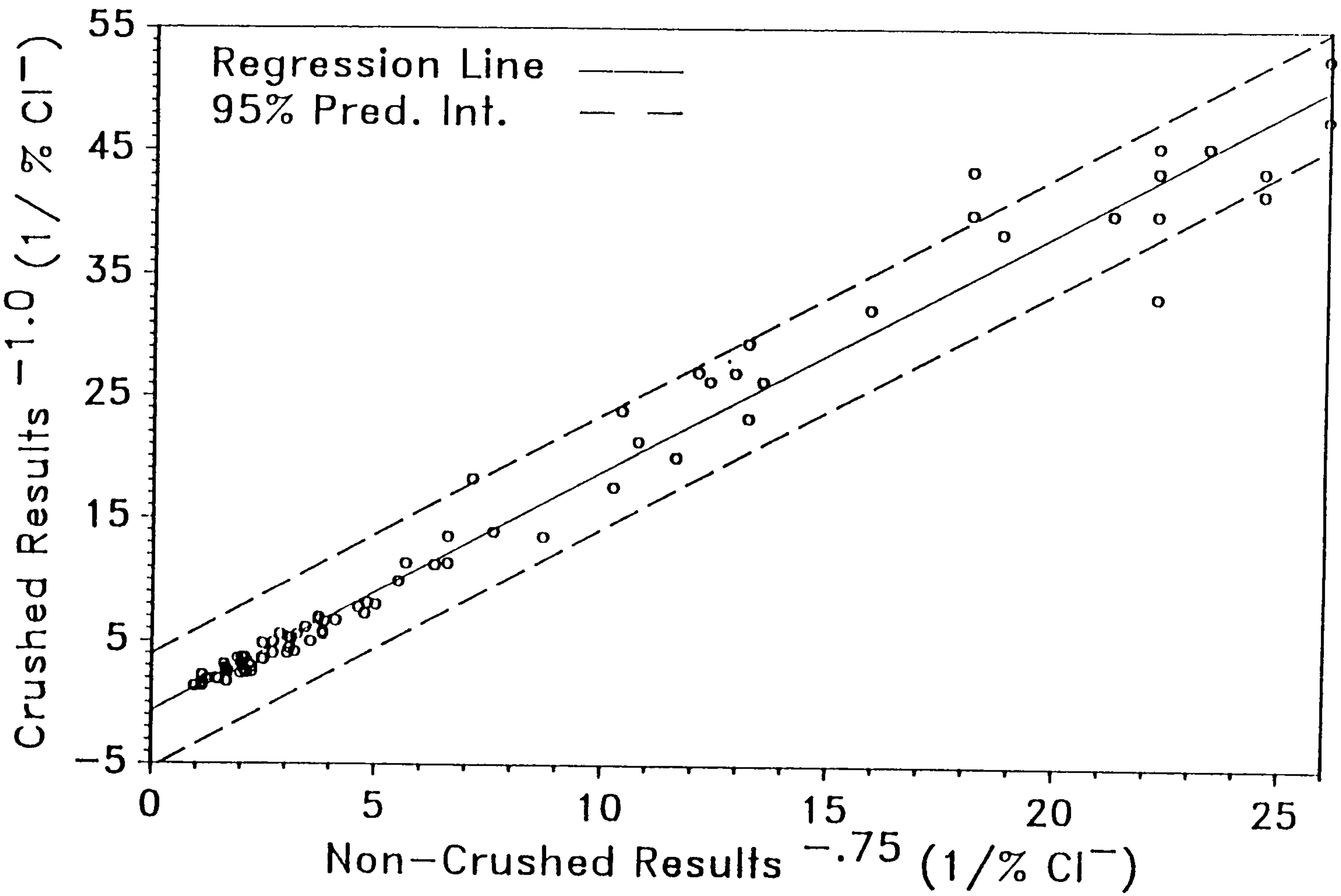


Figure 4-4. Crushed versus uncrushed sample results using specific ion probe.

Results of the regression analysis indicate that the estimated value for the slope is significantly different from 0 at the 5-percent level of significance, while the intercept is not. The coefficient of determination, R^2, indicates that 95.4 percent of the variation in TITR% can be predicted from the independent variable $NOTCR^{0.8}$. The results of the analysis of variance indicate that the error sum of squares for the predicted values is small in relation to the error sum of squares for the regression.

The regression analysis indicates that a strong relationship exists between the results from the standard potentiometric titration procedure and the results obtained from tests conducted with the specific ion probe on uncrushed samples. A plot of the results obtained for the uncrushed samples using the specific ion probe as a function of the potentiometric titration results and the 95-percent confidence limits for the prediction interval is presented in Figure 4-5.

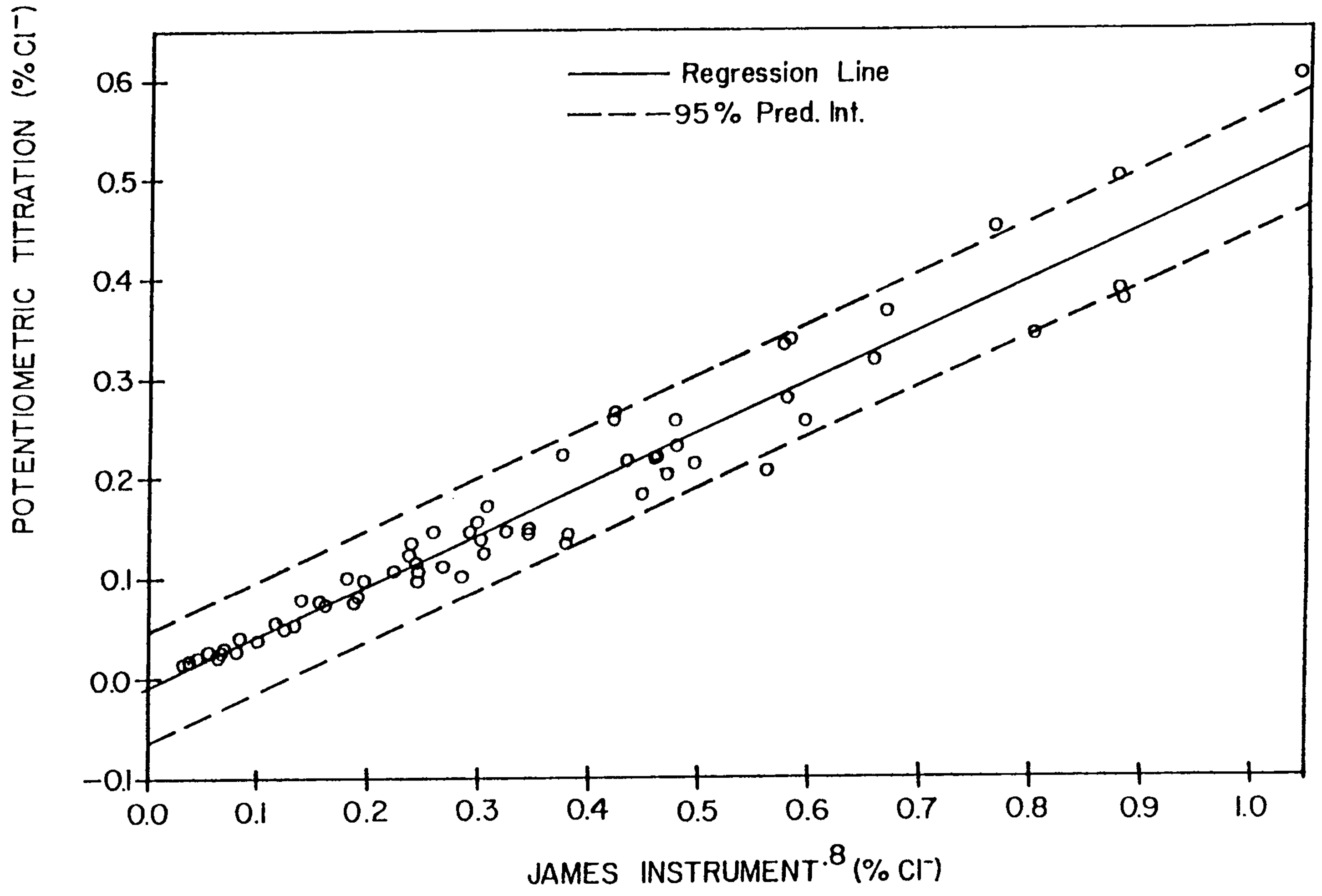


Figure 4-5. Potentiometric titration versus specific ion probe for uncrushed samples.

5

Method Enhancement Studies

Needs

The present standard method for the determination of the chloride content of concrete, AASHTO T260-84, is too laborious and costly to be used to assess the present chloride contamination level of concrete bridges. In Chapter 3 of this volume, four alternative methods were investigated. It was concluded that the specific ion probe method was the most viable for both field and laboratory testing of powdered concrete samples. The procedure was shown to be accurate, fast and economical. However, the chloride measurement process is temperature-dependent, with the rise in temperature of the extraction solution being a function of the type of the coarse aggregate. The acidic extraction solution reacts more vigorously with basic aggregates such as limestone, which results in higher temperatures during measurement. Some means of temperature compensation, then, needs to be applied to determine the standard chloride content equivalence. Also, at chloride contents greater than 0.5 percent, the variability of the chloride measurements increases. Furthermore, the proprietary concrete digestion solution is relatively expensive. A generic solution would ensure that the procedure could always be done on a single, common basis.

Objectives and Scope

The objectives of the enhancement studies are to develop an inexpensive digestion solution and improve the accuracy of the measurement procedure, especially at higher chloride contents. The procedure should be sufficiently accurate to permit the chloride content measurements to be used to determine the chloride diffusion constant for individual bridge components.

The scope of the work presented in this chapter is limited to developing a chloride digestion solution and procedure for measuring the chloride content of powdered concrete samples using a specific chloride probe and potentiometer. The scope includes the following activities:

- Selecting a chloride ion specific probe;
- Selecting a potentiometer;
- Developing a powdered concrete digestion solution;
- Expanding the calibration range for the chloride specific ion probe;
- Validating the revised chloride measurement procedure using powdered concrete samples taken from bridges in Florida, Virginia, Pennsylvania, and Wisconsin; and
- Determining the influence of operator variance for the developed chloride measurement procedure.

Generic Equipment Specifications

The approach used to accomplish the objectives here was to search for commercially available specific chloride probes and compatible potentiometers. In order to be useable in the field and the laboratory, the probe must:

- Be rugged (able to withstand accidental falls);
- Be a self-contained unit having its own reference junction;
- Be resistant to acidic solutions;
- Require little expertise to maintain;
- Have a chloride solution detection range from 0.001- to 1.25-percent chloride.

The potentiometer must:

- Be rugged and portable;
- Have a battery operating life of at least 1000 hours;
- Have a range of ± 2 V with a resolution of 1 mV in the ± 200 mV region;
- Have input impedance greater than 20 MΩ;
- Have a temperature measurement function (Type K or T thermocouple) with a resolution of 1 °F (0.5 °C).

A search of the commercial literature disclosed only one manufacturer of a chloride ion probe meeting the project criteria, Orion Research, Inc., Boston, MA. The Orion combination chloride probe, model 9617B, is a solid-state probe requiring no reference probe. The polymer body is acid resistant with operating pH and temperature ranges of 2 to 12 and 50°F to 122°F (10°C to 50°C), respectively. Chloride solution concentration measurement range is 0.00018 to 3.5 percent. For comparison purposes, chlorides in a digested 3.0-g powdered concrete sample, diluted in a 100-ml solution having a measured chloride content of 0.00018 percent would be equivalent to 0.24 lb Cl/yd^3 (0.14 kg/m^3) concrete, whereas 50 lb Cl/yd^3 (29.75 kg/m^3) of concrete would be a 0.0375-percent solution.

It must be stated that the presence of OH^-, S^-, Br^-, I^-, and CN^- in the final measurement solution will interfere with the chloride specific ion probe's measurement of chlorides present in the solution. Therefore, the test method may not accurately determine the chloride content of concrete made with aggregates that contain pyrite, for example.

A search of the commercial literature disclosed several manufacturers who make a potentiometer that meets the requirements. One is Beckman Industrial Corporation, San Diego, CA. The Beckman model 110T was used for this project. It has input impedance of 22 MΩ, resolution of 0.1 mV in the ± 200 mV DC range and 1 mV in the ± 2 V range. It is rugged (able to withstand accidental falls), has a waterproof case, an operating life of 2000 hours on one standard 9-V battery, and a Type K thermocouple input for temperature measurements to the nearest 1 °F (0.5 °C).

Digestion Solution

The digestion solution was identified as requiring two independent chemical components. The fundamental solution must be an acid of sufficient concentration to digest the powdered concrete samples that is not a chloride derivative and does not present a hazardous environment for operators. It was observed in the earlier work that concretes containing certain basic aggregates produced excessive foaming when introduced into the digestion solution. Thus, a second chemical needed to be added to the solution to reduce the amount of reaction effervescence. Finally, the optimum digestion solution volume needed to be established.

The developed digestion solution was evaluated using one powdered concrete sample selected from each of the Florida, Virginia, Pennsylvania, and Wisconsin bridge component samples. The four samples contained variate chloride contents. Three 0.1-oz (3.0-g) samples were taken from each powdered concrete sample, the potentiometer was turned on, and the chloride probe was calibrated. After about 3 minutes, the chloride probe was placed in the digested sample, and the millivolt reading was recorded after it stabilized. Table 5-1 presents the millivolt readings, the calculated percent chlorides using the calibration equation, the adjusted percent chlorides (which account for the increase in solution volume), and the standard titrated percent chlorides for three solution volumes: 0.34, 0.68, and 1.01 fl oz. (10, 20, and 30 ml). In addition, the means, variance, and coefficients of variation are presented in Table 5-1.

It was noticed that the increase in digestion solution volume increases the amount of chloride ions extracted from the powdered concrete sample in comparison to the 0.34-fl oz (10-ml) volume. The mean percent increases in extracted chlorides from the 0.34- to 0.68-fl oz (10- to 20-ml) and from the 0.34- to 1.01-fl oz (10- to 30-ml) means were 6.4 and 10.6 percent, respectively. The same results are shown in Figure 5-1, where the representative curves of the 0.68 and 1.01 fl oz (20- and 30-ml) solutions were closer to the equivalence line than the 0.34-fl oz (10-ml) set.

An increase from 0.68 to 1.01 fl oz (20 to 30 ml) was concluded to be inappropriate for analysis because the 1.01-fl oz (30-ml) solution required excessive amounts of material for a marginal 4.0 percent increase in the mean chloride contents. However, the improvement in released chlorides for the 0.68-fl oz (20-ml) solution was deemed appropriate for doubling the extraction solution volume. Thus, a volume of 0.68 fl oz (20 ml) of the chloride extraction solution was selected for analysis of 0.1-oz (3.0-g) powdered concrete samples.

Table 5-1. Specific chloride ion probe measured chloride content of powdered concrete samples digested in three different chloride extraction solution volumes.

Volume 10 mL

Sample	Millivolt Reading	Temperature (°F)	Calculated %Cl	Adjusted %Cl	AASHTO Method %Cl
A	1.8	82	0.146	0.146	0.150
B	31.8	82	0.020	0.020	0.023
C	33.4	86	0.018	0.018	0.082
D	57.2	86	0.004	0.004	0.010
Mean	0.047				
Variance	0.003				
Coef. Var.	0.071				

Volume 20 mL

Sample	Millivolt Reading	Temperature (°F)	Calculated %Cl	Adjusted %Cl	AASHTO Method %Cl
A	11.4	78	0.077	0.153	0.150
B	41.9	80	0.010	0.020	0.023
C	40.2	81	0.011	0.022	0.082
D	60.5	82	0.003	0.006	0.010
Mean	0.050				
Variance	0.004				
Coef. Var.	0.071				

Volume 30 mL

Sample	Millivolt Reading	Temperature (°F)	Calculated %Cl	Adjusted %Cl	AASHTO Method %Cl
A	17.4	77	0.051	0.154	0.150
B	45.2	79	0.008	0.024	0.023
C	44.5	80	0.008	0.025	0.082
D	68.0	81	0.002	0.005	0.010
Mean	0.052				
Variance	0.004				
Coef. Var.	0.068				

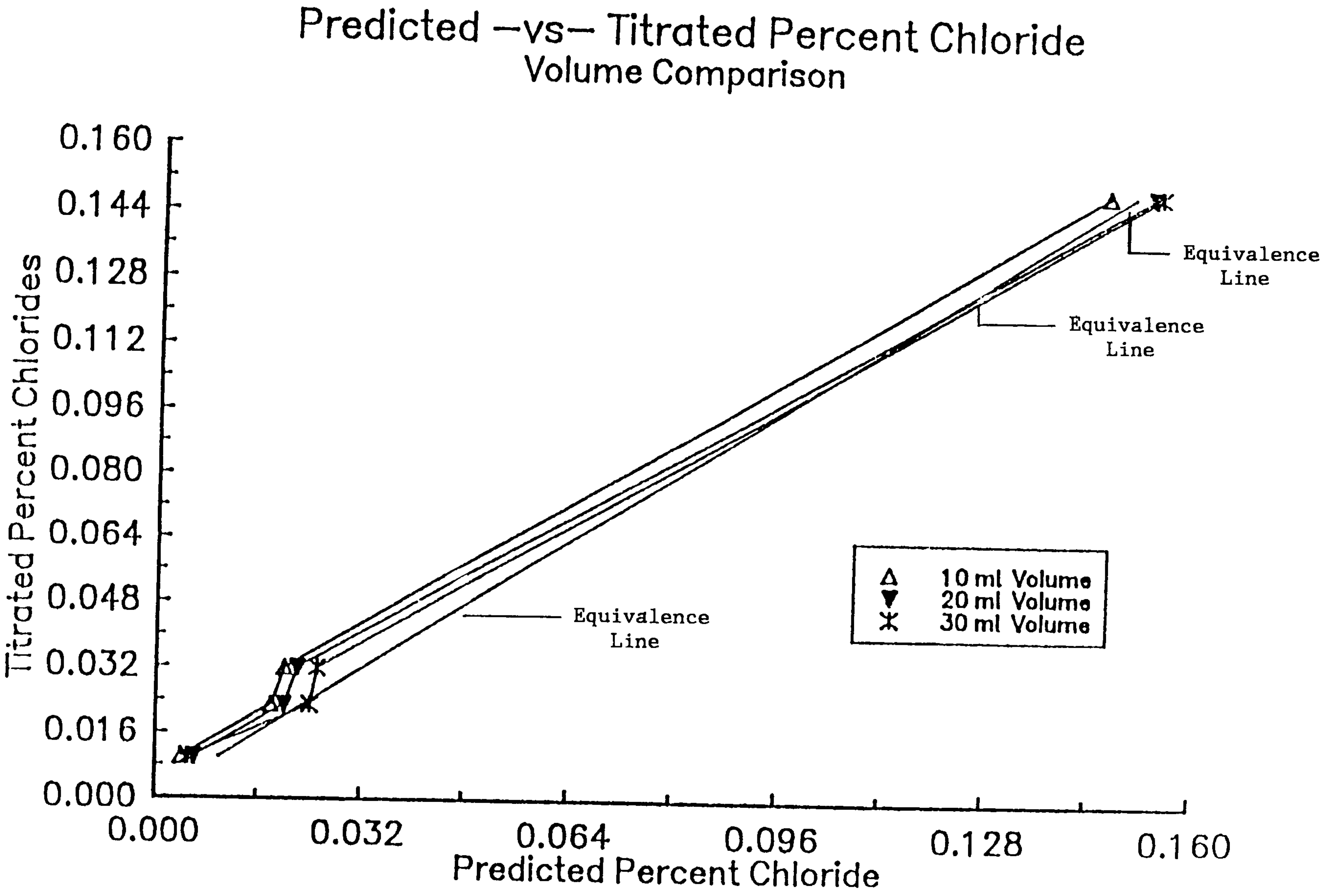


Figure 5-1. Equivalence of predicted and titrated chloride contents for three extraction solution volumes.

Stabilizing Solution

In the earlier work, reported in Chapters 2 and 3, it was observed that as the concrete aggregates became more basic (increased content and purity in limestone) the temperature of the digestion solution increased when the millivolt measurement was taken due to chemical reaction. Also, the time period required for the final stabilized millivolt reading tended to be too variable. Thus, a second (stabilizing) solution was developed and added to the 10-, 20-, and 30-ml extraction solutions at a ratio of 1:3. The final volumes were then 40, 80, and 120 ml. Millivolt readings were taken for the increased volume of chloride extraction solution. Table 5-2 presents the calculated, adjusted for extraction solution volume, and titrated chloride contents for the 40-, 80-, and 120-ml volumes for four samples. In addition, the temperature at measurement time is recorded. The mean, variance, and coefficient of variation for the adjusted percent chloride results are also presented in Table 5-2.

Determining the effectiveness of the additional stabilizing solution on the dispersement of the digestion reaction temperature was the primary objective of the test. During 10-, 20-, and 30-ml measurements, the average measured reaction temperatures increased by 16.7, 11.5, and 10.1 percent for the respective volumes from a room temperature of 72°F (22°C) (see Table 5-1). Although the effective temperatures decreased as the volumes increased from 10 to 30 ml, the marginal decrease was less than 40 percent. The addition of the stabilizing solution affected the temperature to a greater extent (see Table 5-2). The temperatures decreased by an average of 58 percent from the initially increased reaction temperatures. The final temperatures, in comparison to room temperature, were increased by 6.9, 4.5, and 4.5 percent for 40, 80, and 120 ml.

Figure 5-2 presents an equivalence comparison for the 40-, 80-, and 120-ml predicted percent chlorides and the standard titrated chloride contents. As shown, the 80- and 120-ml curves are significantly closer to the equivalence line than the 40-ml curve. In fact, the 120-ml curve almost coincides with the equivalence line. The improvement in the equivalence between the predicted and the standard chloride content is a combination of a reduction in temperature to near room temperature and a decrease in solution chloride concentration. Also, since the specific ion probe measures the relative chloride concentrations in solution, the probe's measuring performance improves as the higher chloride levels are diluted into a lower range.

Thus, the final powdered concrete chloride extraction solution for measuring the in situ chloride content of concrete was increased to 1:4--20 ml of the acid-based digestion solution followed by 80 ml stabilizing solution for a 3.0-g powdered concrete sample.

Table 5-2. Effects of addition of a stabilizing solution to the 10-, 20-, and 30-ml chloride extraction solutions at a constant ratio of 1:3.

Volume 40 mL

Sample	Millivolt Reading	Temperature (°F)	Calculated %Cl	Adjusted %Cl	AASHTO Method %Cl
A	30.6	76	0.021	0.170	0.150
B	59.6	77	0.003	0.024	0.023
C	52.0	77	0.005	0.040	0.082
D	77.5	78	0.001	0.007	0.010
Mean	0.060				
Variance	0.004				
Coef. Var.	0.068				

Volume 80 mL

Sample	Millivolt Reading	Temperature (°F)	Calculated %Cl	Adjusted %Cl	AASHTO Method %Cl
A	43.9	75	0.009	0.139	0.150
B	71.9	75	0.001	0.021	0.023
C	66.0	75	0.002	0.032	0.082
D	84.2	76	0.001	0.009	0.010
Mean	0.050				
Variance	0.003				
Coef. Var.	0.053				

Volume 120 mL

Sample	Millivolt Reading	Temperature (°F)	Calculated %Cl	Adjusted %Cl	AASHTO Method %Cl
A	48.8	74	0.006	0.150	0.150
B	75.5	76	0.001	0.025	0.023
C	71.2	75	0.001	0.034	0.082
D	84.5	76	0.001	0.014	0.010
Mean	0.056				
Variance	0.003				
Coef. Var.	0.055				

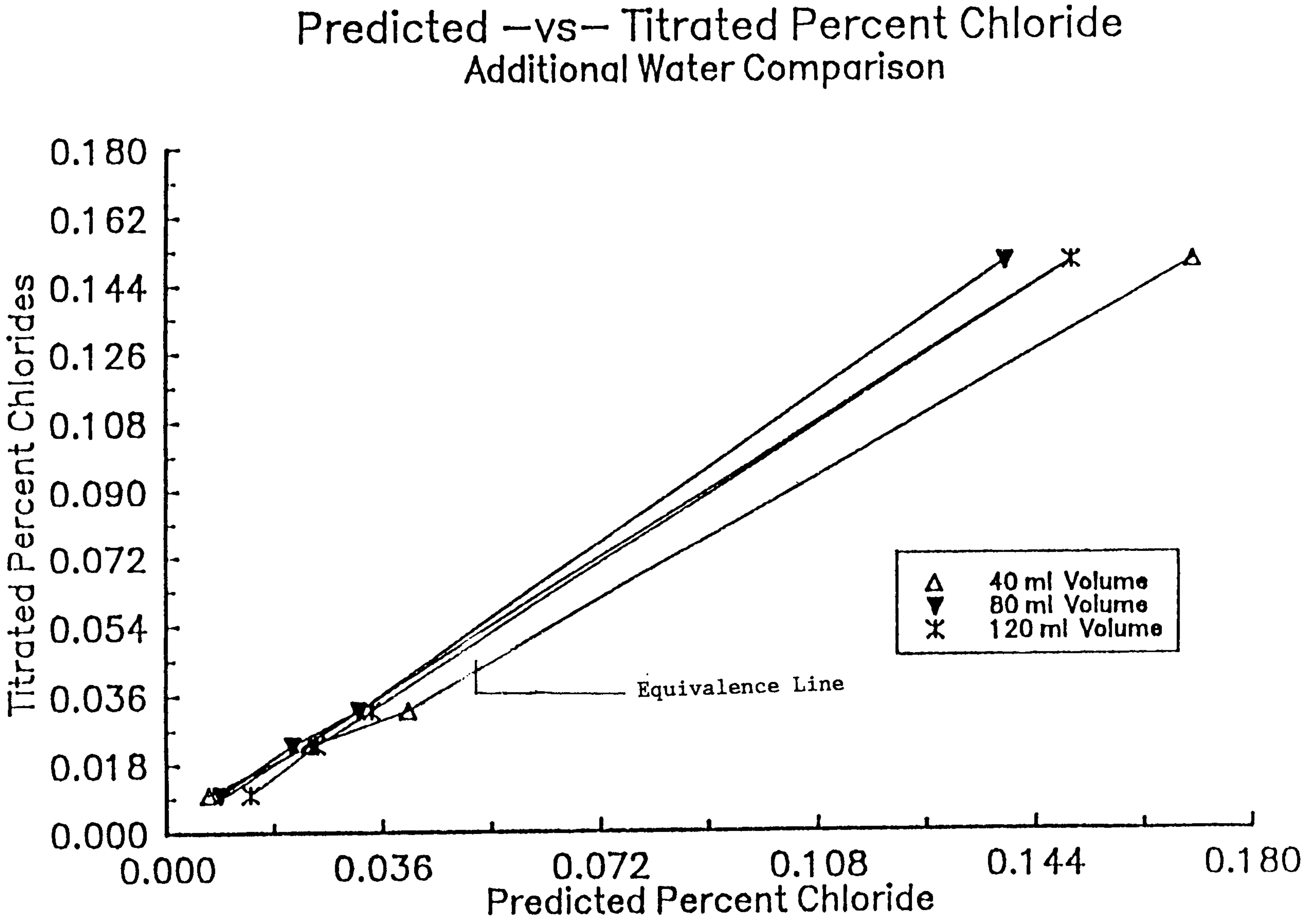


Figure 5-2. Equivalence of predicted and titrated chloride contents of the extraction solution diluted by a ratio of 1:3.

The revised chloride extraction-measurement procedure, then, becomes:

1. Weigh 3.0 g of powdered concrete sample as taken by the vacuum-carbide bit sampling method.

2. Place the 3.0-g sample in 20 ml of acid-based extraction solution in a 125-ml plastic bottle, cover the bottle and shake vigorously to suspend the powder in the solution, and let the powder digest for 3 minutes.

3. Carefully remove the top of the bottle (container may become pressurized during the digestion period). Add 80 ml of the stabilizing solution to the 3.0-g powdered concrete sample digested in the 20 ml-digestion solution. Replace the cap on the 150 ml bottle, shake vigorously for 1 minute, remove the top in the bottle, place the probe to a depth of mid-height in the extraction solution, wait 2 minutes, and record the stabilized millivolt reading. A millivolt reading is stable when the oscillation is less than $\pm$ 0.5 mV.

Expanded Calibration Range

In the work reported in Chapters 3 and 4, the calibration solutions used were 0.005, 0.05, and 0.5 percent, which correspond to approximately 0.2, 2.0, and 20 lb Cl/yd^3 (0.1, 1.2, and 11.9 kg Cl/yd^3) concrete. Further, it was noted that the variability of chloride contents from predicted results increased as the chloride contents increased above the maximum calibration solution concentration of 0.5 percent. Therefore, the calibration solution range was increased in an effort to reduce the increased variability of results at higher chloride concentration levels. Five concentrations were selected in the range of 0.01- to 1.25-percent chlorides (0.01, 0.03, 0.3, 0.6, and 1.25 percent). Thus, the calibration solutions included a range of chloride content of about 0.4 to 50 lb Cl/yd^3 (0.2 to 29.8 kg/m^3) concrete. Table 5-3 presents the recorded millivolt readings for different probe-potentiometer combinations.

The five new calibration solutions were analyzed based on a linear representation of the logarithm (base 10) of the chloride concentrations with the millivolt readings. A general comparison to the old triple level concentration sets was also made. The results of the linear regression analysis are presented below.

Table 5-3. Calibration solution millivolt readings using different probe-potentiometer combinations for the original and new solutions.

Original Calibration Solutions

Concentration	Millivolt Reading
0.5 %Cl	-5.3
0.05 %Cl	51.4
0.005 %Cl	104.8

New Calibration Solutions

Concentration	Millivolt Reading
1.25 %Cl	-30.6
0.6 %Cl	-20.3
0.3 %Cl	-10.4
0.03 %Cl	24.0
0.01 %Cl	40.5

For the 5-level new calibration series:

$$\text{LOG Y} = -0.815327 - 0.0293951 \text{ mV} \qquad (5\text{-}1)$$

where

LOG Y = $\log_{10}$ of the chloride concentrations (in %), and
mV = millivolt readings

For the 3-level original calibration series:

$$\text{LOG Y} = -0.38759 - 0.0181599 \text{ mV} \qquad (5\text{-}2)$$

The coefficients of determination (R^2) are 100 percent and 99.9 percent, respectively, and evaluations of the coefficients in the equations revealed them all to be significant.

Both equations 5-1 and 5-2 are substantial representations of the millivolt responses recorded. The slope of equation 5-1 is slightly greater than the slope of equation 5-2 because of the increased concentration values. A comparison between the two equations is unfeasible due to instrumentation differences as presented below.

Up to this point, a calibration equation was determined for the probe-potentiometer combination every time the instrument was turned on and a new set of chloride measurements were taken. In this study, an effort was extended to develop a calibration equation for a given chloride instrument (a unique combination of chloride probe-potentiometer). Eighteen sets of the extended five calibration readings were taken for a single instrument over a 6-month period (see Table 5-4). The following presents the results of a linear regression analysis of the calibration reading presented in Table 5-4:

$$\text{LOG Y} = -0.724473 - 0.030925 \text{ mV} \qquad (5\text{-}3)$$

Here R^2 = 98.9 and two-sided t-tests reveal the coefficients to be nontrivial. Figure 5-3 presents equation 5-3 and its 95-percent confidence limits.

The dynamic effects of the statistical test fall within two categories. The first category is the repeatability of the readings. The regression analysis concluded that 98.7 percent of the

Table 5-4. Chloride solution calibration readings for chloride instrument number one.

	Solution Concentration				
Observation	0.01	0.03	0.3	0.6	1.25
1	42.2	25.4	-10.1	-19.8	-29.0
2	40.5	24.0	-10.4	-20.3	-30.6
3	41.1	24.6	-9.7	-19.5	-30.0
4	37.3	21.7	-11.5	-21.3	-31.5
5	42.6	26.1	-6.9	-16.7	-27.4
6	39.7	24.3	-7.0	-15.4	-24.1
7	41.2	24.8	-9.5	-19.3	-29.7
8	42.0	26.5	-5.9	-14.3	-24.6
9	42.5	26.7	-6.6	-15.6	-26.7
10	44.3	27.8	-7.4	-17.2	-28.5
11	37.0	21.6	-11.3	-20.0	-30.9
12	46.6	29.4	-6.6	-16.4	-28.3
13	42.9	28.4	-3.1	-11.9	-21.4
14	43.4	28.2	-3.4	-12.4	-21.7
15	42.9	28.0	-4.2	-13.3	-23.0
16	43.3	27.9	-4.5	-13.3	-24.0
17	43.3	28.0	-4.5	-13.3	-24.1
18	42.8	27.8	-4.7	-13.4	-23.7

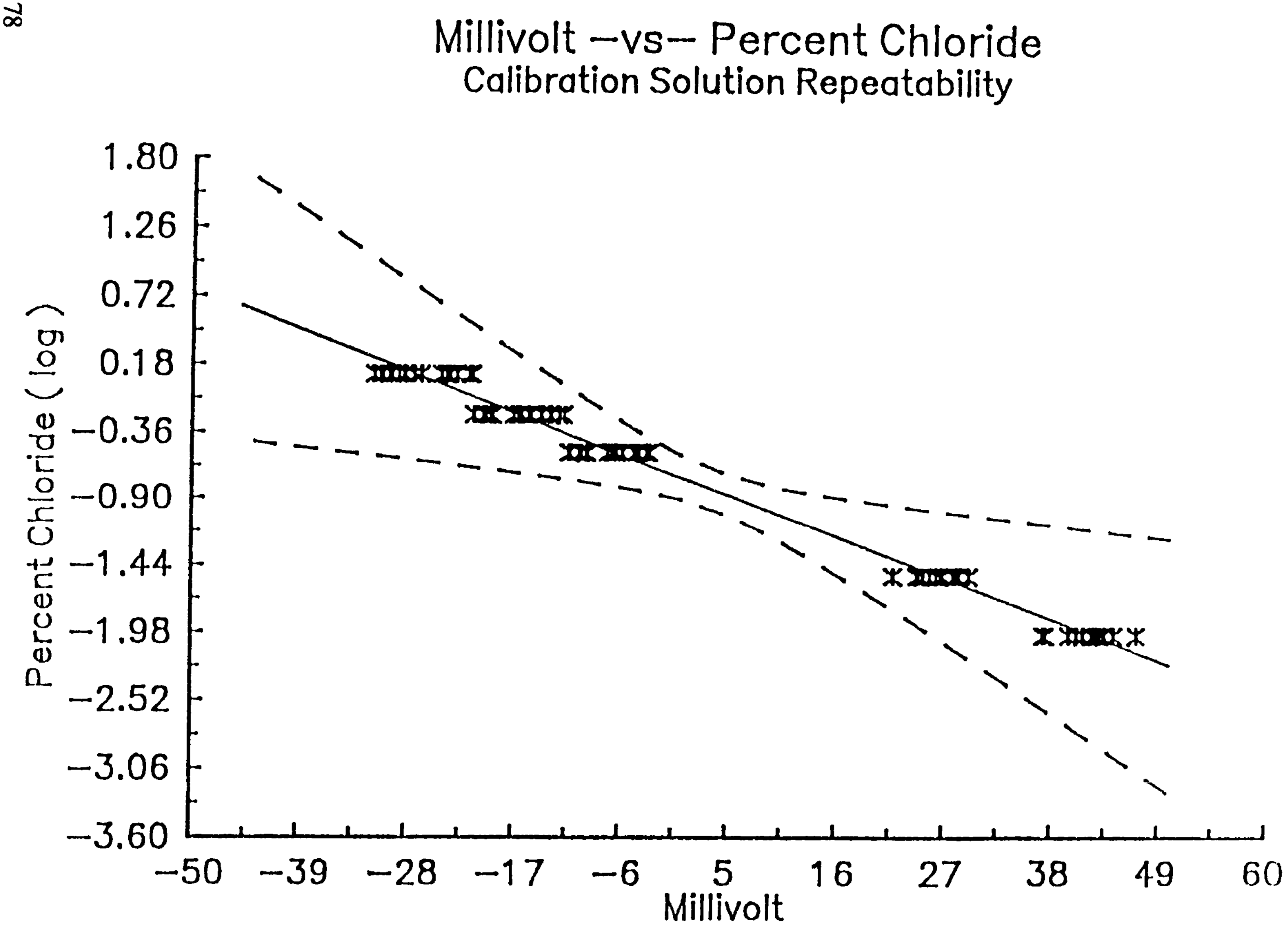


Figure 5-3. Calibration equation for chloride instrument number 1 and the 95-percent confidence limits.

predicted values were represented by the linear equation. Since the compiled readings were comprised of multiple operators, the effective conclusion suggests the elimination of the use of calibration solutions preceding every initiation of the equipment. The elimination of the solutions does not significantly affect the final analysis as revealed by the high R^2 value.

The researchers are not suggesting the total elimination of the calibration solutions. Since the probe has an approximate life span of 1 year in normal laboratory usage (as stated by the manufacturer), the probe will eventually begin to incorrectly respond to chloride concentrations. Therefore, it is suggested that periodic readings be taken on the calibration solutions to monitor the effectiveness of the equipment and to determine the end of the probe's useful life.

The second category is the application of the repeatability in the formulation of a unique equation for each chloride instrument (probe and meter combination). Currently, an operator calculates a predicted percent chloride content in a concrete sample from a calibration equation that is determined each time the instrument is turned on to test a set of samples.

An additional step involves transforming the predicted values to the representative AASHTO equivalence by an alternative equation as suggested in Chapter 4.

In summary, the unique calibration solution equation totally eliminates the initial step of determining a particular calibration each time the instrument is turned on. Regression of at least five sets of calibration solution readings adequately produces the linear representation of a chloride instrument. The linear calibration equation incorporated into an AASHTO equivalence equation produces a millivolt transformation equation applicable to any concrete chloride analysis made using the specified chloride instrument.

As discussed, a single calibration equation can be developed for a probe-potentiometer combination. However, it needs to be determined whether the calibration equation is unique for a probe or a probe-potentiometer combination. Thus, calibration equations were developed for two meters (No. 1 and No. 2) and two probes (No. 1 and No. 2). The millivolt readings from the five calibration solutions (0.01-, 0.03-, 0.3-, 0.6-, and 1.25-percent chlorides) are presented in Table 5-5.

An analysis of variance between meters, probes, solution concentration, meter-probe (M*P), meter-concentration (M*C), probe-concentration (P*C) and meter-probe-solution concentration (M*P*C) is presented below:

Table 5-5. Millivolt readings from calibration solution for meter and probe combinations.

							Calibration Solution %Cl
Meter 1							
Probe 1							
	42.9	43.4	42.9	43.3	43.3	42.8	0.01
	28.4	28.2	28.0	27.9	28.9	27.8	0.03
	-3.1	-3.4	-4.2	-4.5	-4.5	-4.7	0.3
	-11.9	-12.4	-13.3	-13.3	-13.3	-13.4	0.6
	-21.4	-21.7	-23.0	-24.0	-24.1	-23.7	1.25
Probe 2							
	41.5	42.5	39.0	40.0	37.4	37.4	0.01
	25.1	25.4	23.9	24.1	22.5	22.5	0.03
	-8.7	-7.6	-10.6	-9.6	-6.7	-8.6	0.3
	-18.2	-16.7	-20.3	-18.7	-15.2	-17.5	0.6
	-28.0	-26.4	-30.2	-30.0	-26.0	-28.7	1.25
Meter 2							
Probe 1							
	72.6	72.2	71.9	71.6	71.2	71.8	0.01
	45.6	45.5	45.4	45.3	45.3	45.4	0.03
	-9.3	-9.8	-9.3	-10.2	-10.0	-10.2	0.3
	-26.0	-25.8	-25.6	-25.6	-25.4	-25.4	0.6
	-42.1	-42.1	-42.5	-44.0	-43.5	-43.5	1.25
Probe 2							
	72.2	72.4	72.7	66.9	70.3	71.2	0.01
	45.5	45.5	45.8	41.3	43.5	44.7	0.03
	-10.0	-10.2	-9.7	-14.6	-12.7	-11.8	0.3
	-26.3	-26.3	-26.0	-29.8	-28.4	-27.8	0.6
	-42.8	-42.4	-42.3	-47.7	-46.9	-46.1	1.25

Source	Mean Square	F_c Value	P Value	F_b Value
Meter	268.502	129.31	.0001	3.95
Probe	250.274	120.53	.0001	3.95
Concentration	35907.184	17293.14	.0001	2.48
M*P	58.281	28.12	.0001	3.95
M*C	2566.266	1235.93	.0001	2.48
P*C	1.081	0.52	.7209	2.48
M*P*C	0.201	0.10	.9833	2.48

Statistically, the F-values represent the distribution of the independent random variables contained within a Chi-squared distribution. For hypothesis acceptance, the calculated values must not exceed the critical tabulated values, which indicates insignificant variation among the means. The two hypotheses being tested are:

Hypothesis: $\alpha_1 = \alpha_2 = \ldots = \alpha_n = 0$
Alternative: at least one α is not equal to zero

Hypothesis: $(\alpha\beta)_{11} = (\alpha\beta)_{12} = \ldots = (\alpha\beta)_{nm} = 0$
Alternative: at least one $(\alpha\beta)$ is not equal to zero

The meters and the probes were analyzed by comparing the F-values and using the first hypothesis. The meters displayed significant differences although they were not predicted to be completely independent. Prior to the investigation, both meters were calibrated against a high resolution source and displayed identical millivolt responses for a given voltage. The results suggested that the configuration used uniquely affected the true electrical circuitry of each meter. The millivolt responses were not incorrect for each combination; rather, they were skewed about a point due to the particular electrical responses associated with the particular meter.

The probe analysis also resulted in significant differences in the mean effects. Again, the difference was unexpected since both probes were purchased from the same manufacturer. Although the results of the probe test signified differences, it was noticed that the true differences were associated with the meters rather than the probes.

The results of the concentration levels were irrelevant on an individual basis. The solutions contained variate chloride levels and were used primarily for testing adaptivity.

Using the second hypothesis and comparing the F-values, the effects of the meter and probe, meter and concentration, probe and concentration, and meter, probe, and solution concentration combination were studied. The three alternatives were analyzed for combination adaptivity. The F-values for the combination of the meter and probe were determined to be significantly different. The two components failed to disprove the independence of the meters in an additive arrangement. In essence, the combinations of meters and probes reinforced the conclusion drawn from the results from the independent meter. Again, the resulting millivolt readings were dependent on the meter and were unique for variate meter/probe combinations.

In comparing the probe and concentration levels, insignificant differences were observed for the variate combinations. Once again, the principle of meter-created differentials was proven, because the probes performed the assigned tasks without differences in the mean mV readings.

The significance of the analysis is represented in the comparison of the F-values for the combinations of the meters, probes, and concentrations. The F-values concluded that the additive effects of the three components were significant. The results justify the principle that, regardless of the intermediate meter effects, all meter and probe combinations represent similar final results. Although the results of the combinations are similar, the representation of the millivolt readings are unique for each specific combination. Identical meters give similar results, but differently manufactured and specified meters produce different millivolt readings. In other words, calibration equations for one combination are not suitable for other meter and probe combinations.

Calibration Equations for Revised Procedure

Millivolt readings were taken using two fixed probe meter combinations (FPMC A and FPMC B), which were calibrated using the five solution (expanded range) calibration series. Prior to the measurement, a 3.0-g sample of crushed concrete was weighed on a triple beam balance. The weighed sample was placed in a 125-ml nalgene bottle containing 20 ml of the digestion solution developed in this research. The bottle was capped and agitated for approximately 1 minute. Approximately 3 minutes after the addition of the concrete, 80 ml of stabilizing solution was mechanically added to the 20-ml volume. The chloride probe and a thermocouple were inserted into the solution following agitation of the final volume. Stable millivolt and temperature responses were recorded in a 1- to 2-minute interval after agitation.

To obtain the percent chlorides, equation 5-4, which was statistically obtained from the calibration results, was applied to the millivolt readings.

$$\text{LOG } Y = -0.732531 - 0.0304219 \text{ mV} \tag{5-4}$$

where

LOG Y = $\log_{10}$ of the initial predicted chloride content (percent), and
mV = millivolt reading.

The initial results of the predicted percent chlorides deviated from the actual percent chlorides, which is believed to be due to the influence of the digested concrete residue. The predicted values were adjusted for the suspended and settled materials using equation 5-5.

$$\%\text{Cl} = (10Y + 0.01)^{.99} \tag{5-5}$$

where

%Cl = final predicted chloride content (%), and
Y = initial predicted chloride content from equation 5-4.

The coefficient adjusts for increased volume, while the constant adjusts to the lower percent chlorides. The effect of the reduced exponent is to force the higher percent chlorides closer to the equilibrium line while not greatly affecting the lower concentration levels.

The data obtained and the results of the two equations, 5-4 and 5-5, are presented in Table 5-6. The titrated percent chloride and the final predicted percent chloride relationship are presented in Figure 5-4.

Validation of Revised Procedures Using Field Samples

Validation of the revised procedures was carried out using powdered concrete samples extracted from existing bridge structures in Virginia, Pennsylvania, Wisconsin, and Florida. Twenty samples were chosen randomly from each state's bridge structure to be analyzed. The millivolt readings and the final percent chloride content using the procedures developed in this research are presented in Tables 5-7 through 5-10.

Table 5-6. Chloride content results using equations 5-4 and 5-5 and AASHTO method at 100-ml solution.

Sample	Chloride Content (lb/yd^3)	Millivolt Reading	Temperature (°F)	Initial Predicted %Cl	Final Predicted %Cl	AASHTO Method %Cl
C-0	0	81.6	73	0.0006	0.0168	0.0166
		85.4	74	0.0006	0.0166	
C-1	0.2	76.2	72	0.0009	0.0197	0.0193
		74.8	74	0.0012	0.0229	
C-2	0.4	67.4	72	0.0016	0.0275	0.0274
		71.2	74	0.0015	0.0263	
C-3	0.8	58.5	72	0.0031	0.0421	0.0412
		62.5	74	0.0028	0.0388	
C-4	1.6	57.3	72	0.0033	0.0448	0.0520
		58.3	74	0.0037	0.0480	
C-5	3.2	43.5	72	0.0088	0.1002	0.1026
		46.8	74	0.0079	0.0914	
C-6	6.4	34.7	72	0.0163	0.1759	0.1439
		38.5	73	0.0138	0.1512	
C-7	8.6	30.3	73	0.0222	0.2351	0.2293
		33.7	73	0.0191	0.2043	
C-8	10.8	24.4	73	0.0335	0.3488	0.3143
		26.4	74	0.0312	0.3256	
C-9	12.8	24.5	73	0.0333	0.3465	0.4113
		25.8	74	0.0325	0.3385	
M-1	0	84.6	73	0.0005	0.0156	0.0145
		87.3	74	0.0005	0.0159	
M-2	20.0	27.1	73	0.0277	0.2910	0.2778
		29.3	74	0.0257	0.2703	
M-3	30.0	23.5	73	0.0357	0.3706	0.3439
		26.0	73	0.0320	0.3341	
M-4	50.0	13.1	74	0.0740	0.7517	0.7209
		15.7	74	0.0640	0.6530	

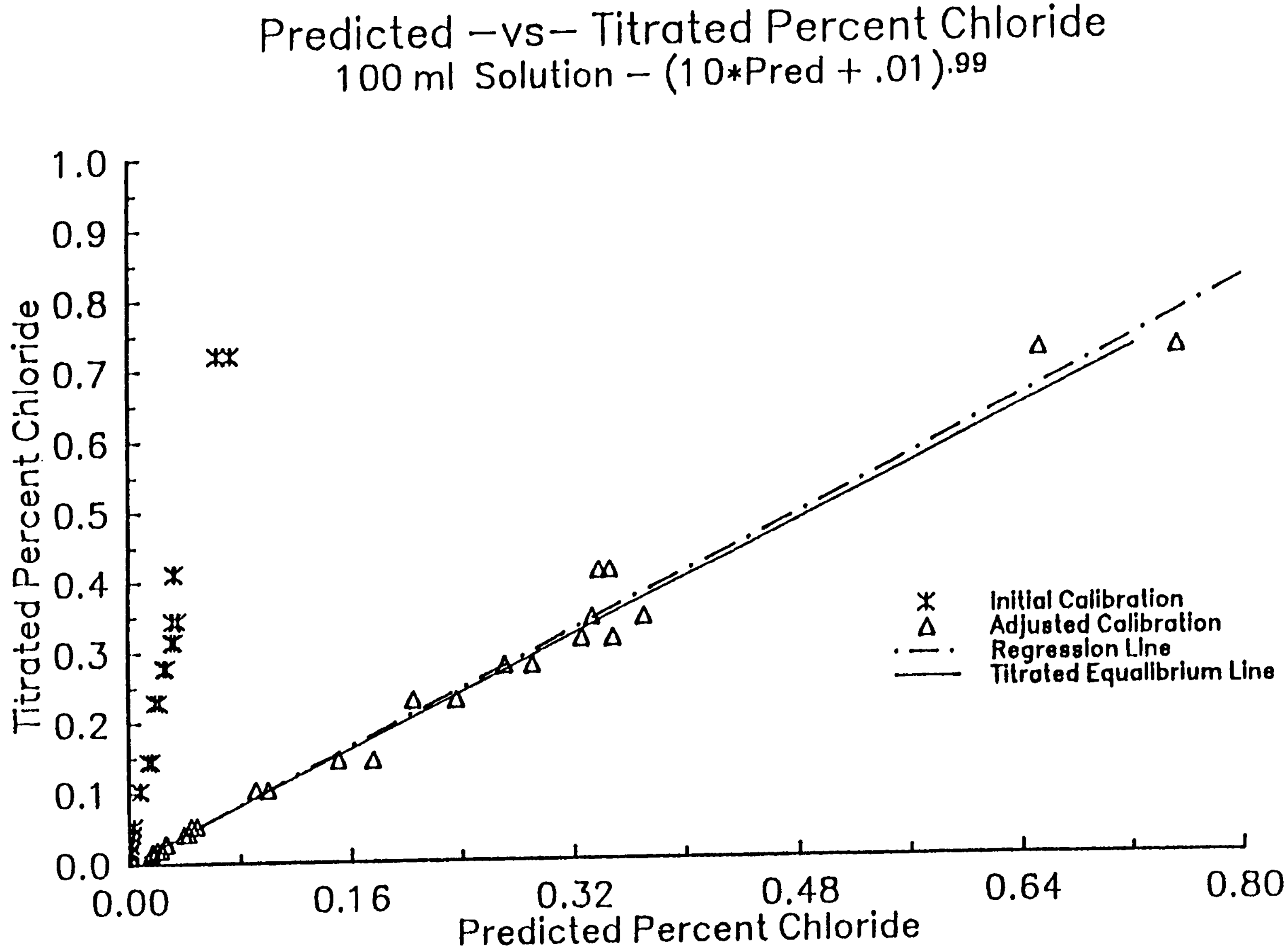


Figure 5-4. The relationship between the titrated percent chloride and the initial predicted percent chloride in 100-ml solution.

Table 5-7. Percent chloride results using the developed procedures for Florida samples.

Sample	Millivolt Reading	Temperature (°F)	Final Predicted %Cl	AASHTO Method %Cl	Chloride Content (lb/yd^3)
B1A-5	87.2	72	0.015	0.004	0.16
B1-5	81.0	71	0.017	0.006	0.24
F1-6	48.2	71	0.078	0.106	4.24
F2-2	19.1	72	0.513	0.503	20.12
F2-3	26.5	72	0.312	0.333	13.32
F2-4	33.1	72	0.202	0.206	8.24
F2-5	31.6	72	0.223	0.231	9.24
F2-6	39.8	72	0.131	0.144	5.76
P1-2	28.3	72	0.277	0.260	10.40
P1-3	34.5	72	0.184	0.170	6.80
P1-4	39.6	72	0.133	0.120	4.8
P1-5	49.4	72	0.073	0.073	2.92
P1-6	64.9	72	0.032	0.026	1.04
P2-3	43.5	71	0.104	0.097	3.64
P2-4	53.5	71	0.057	0.053	2.12
P2-5	61.6	72	0.037	0.025	1.00
P2-6	69.6	72	0.026	0.018	0.72
P3-5	73.6	72	0.022	0.011	0.44
P3-6	80.4	71	0.018	0.055	2.20
DC-5	79.7	72	0.018	0.006	.24
C5-5	83.1	72	0.016	0.006	0.24
P1-5	67.0	72	0.029	0.023	.92

Table 5-8. Percent chloride results using the developed procedures for Pennsylvania samples.

Sample	Millivolt Reading	Temperature (°F)	Final Predicted %Cl	AASHTO Method %Cl	Chloride Content (lb/yd^3)
C1-3	74.9	71	0.021	0.014	0.56
D-1	31.4	72	0.226	0.184	7.36
E-2	68.3	71	0.027	0.023	0.92
P1-3	56.9	71	0.047	0.037	1.48
D-3(11/15)	73.9	71	0.022	0.014	0.56
H-2	60.3	71	0.040	0.038	1.52
P2-1	26.3	72	0.317	0.293	11.72
A-2	52.2	71	0.062	0.007	0.28
A-4	85.9	72	0.015	0.010	0.40
K-4	70.9	72	0.024	0.017	0.68
C2-2	67.8	71	0.028	0.019	0.76
D-3(I80)	81.5	71	0.017	0.009	0.36
K-2	79.1	74	0.018	0.015	0.60
E-4	83.5	74	0.016	0.010	0.40
I-2	71.7	71	0.024	0.018	0.72
B-3	53.2	71	0.058	0.051	2.00
L-2	67.8	71	0.028	0.020	0.80
I-1	35.8	71	0.163	0.185	7.40
A-3	78.0	71	0.019	0.016	0.64
H-2	58.8	71	0.043	0.035	1.40

Table 5-9. Percent chloride results using the developed procedures for Virginia samples.

Sample	Millivolt Reading	Temperature (°F)	Final Predicted %Cl	AASHTO Method %Cl	Chloride Content (lb/yd^3)
A01	29.9	74	.249	.256	10.24
A-2(927)	44.5	73	.098	.096	3.84
A-3	67.3	72	.028	.030	1.20
A-4	80.6	78	.018	.020	0.80
B-1	22.6	76	.406	.389	15.56
B-2	36.5	77	.162	.183	7.32
B-3	33.8	72	.193	.216	8.64
D-1	22.3	73	.414	.386	15.44
D-3	36.3	73	.164	.142	5.68
D-4	42.8	73	.109	.101	4.04
D-5	48.9	72	.075	.074	2.96
I-1	31.2	74	.229	.220	8.80
I-3	56.1	77	.050	.051	2.04
I-4	70.9	77	.024	.021	0.84
K-2	43.0	74	0.107	0.107	4.28
K-4	72.1	77	0.023	0.025	1.00
L-1	29.5	77	0.256	.258	10.32
L-4	61.3	77	.038	.039	1.56
E-2	40.3	77	.127	.134	5.36
A-2(676)	26.5	77	.312	.285	11.40

Table 5-10. Percent chloride results using the developed procedures for Wisconsin samples.

Sample	Millivolt Reading	Temperature (°F)	Final Predicted %Cl	AASHTO Method %Cl	Chloride Content (lb/yd^3)
B-5	55.7	73	0.051	0.067	2.68
A-5	49.8	74	0.071	0.132	5.28
C-3	48.0	74	0.079	0.098	3.92
A2-3	70.7	73	0.025	0.029	1.16
K-1	22.2	73	0.417	0.486	19.44
B-2	43.2	74	0.106	0.118	4.72
F-1	29.5	73	0.256	0.285	11.40
C-2	29.6	76	0.254	0.301	12.04
J-2	23.6	74	0.379	0.445	17.80
L-2	32.1	72	0.216	0.233	9.32
K-3	39.7	73	0.132	0.145	5.80
G-3	28.8	74	0.268	0.279	11.16
D-5	48.1	73	0.079	0.197	7.88
B-6	62.5	74	0.036	0.047	1.88
F-5	65.9	74	0.030	0.036	1.44
D-3	40.3	74	0.127		
E-2	27.1	74	0.300	0.315	12.60
A-3	30.6	74	0.238	0.272	10.84
C-6	65.1	74	0.031	0.037	1.24
I-5	61.9	74	0.034	0.043	1.72

A statistical analysis was performed on the results from each state. Regression equations to verify the relationship between the standard and measured chloride content values for the results from Florida, Pennsylvania, Virginia, and Wisconsin, and all states together are presented in equations 5-6 through 5-10.

Florida Samples

$$(\%Cl)_{standard} = + .992\ (\%Cl)_{measured} \qquad (5\text{-}6)$$

The regression results are also presented in Figure 5-5.

Pennsylvania Samples

$$(\%Cl)_{standard} = + .895\ (\%Cl)_{measured} \qquad (5\text{-}7)$$

The regression results are presented in Figure 5-6.

Virginia Samples

$$(\%Cl)_{standard} = + .967\ (\%Cl)_{measured} \qquad (5\text{-}8)$$

The regression results are presented in Figure 5-7.

Wisconsin Samples

$$(\%Cl)_{standard} = + 1.107\ (\%Cl)_{measured} \qquad (5\text{-}9)$$

The regression results are presented in Figure 5-8.

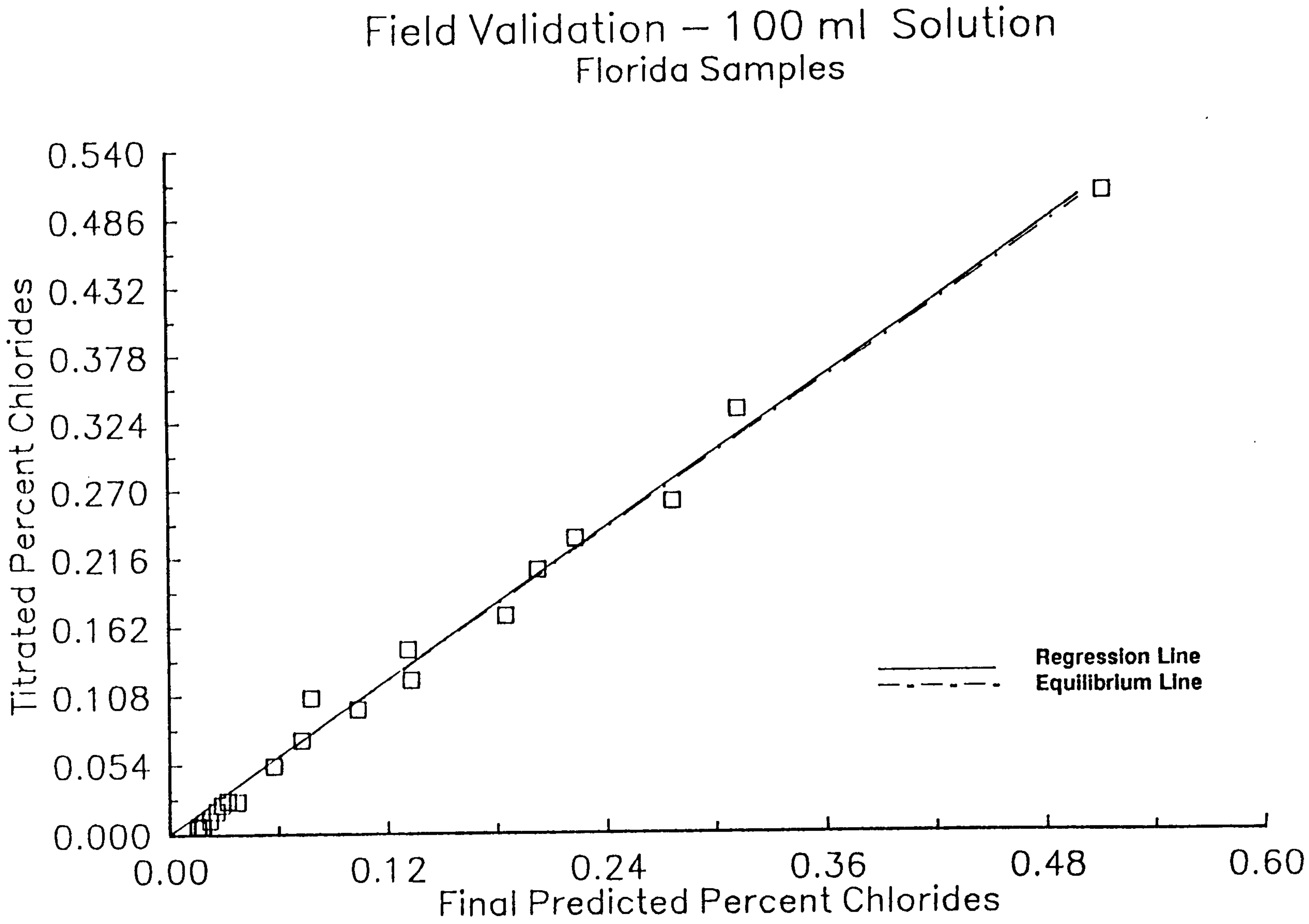


Figure 5-5. The relationship between the chloride contents using the standard and developed methods for Florida samples.

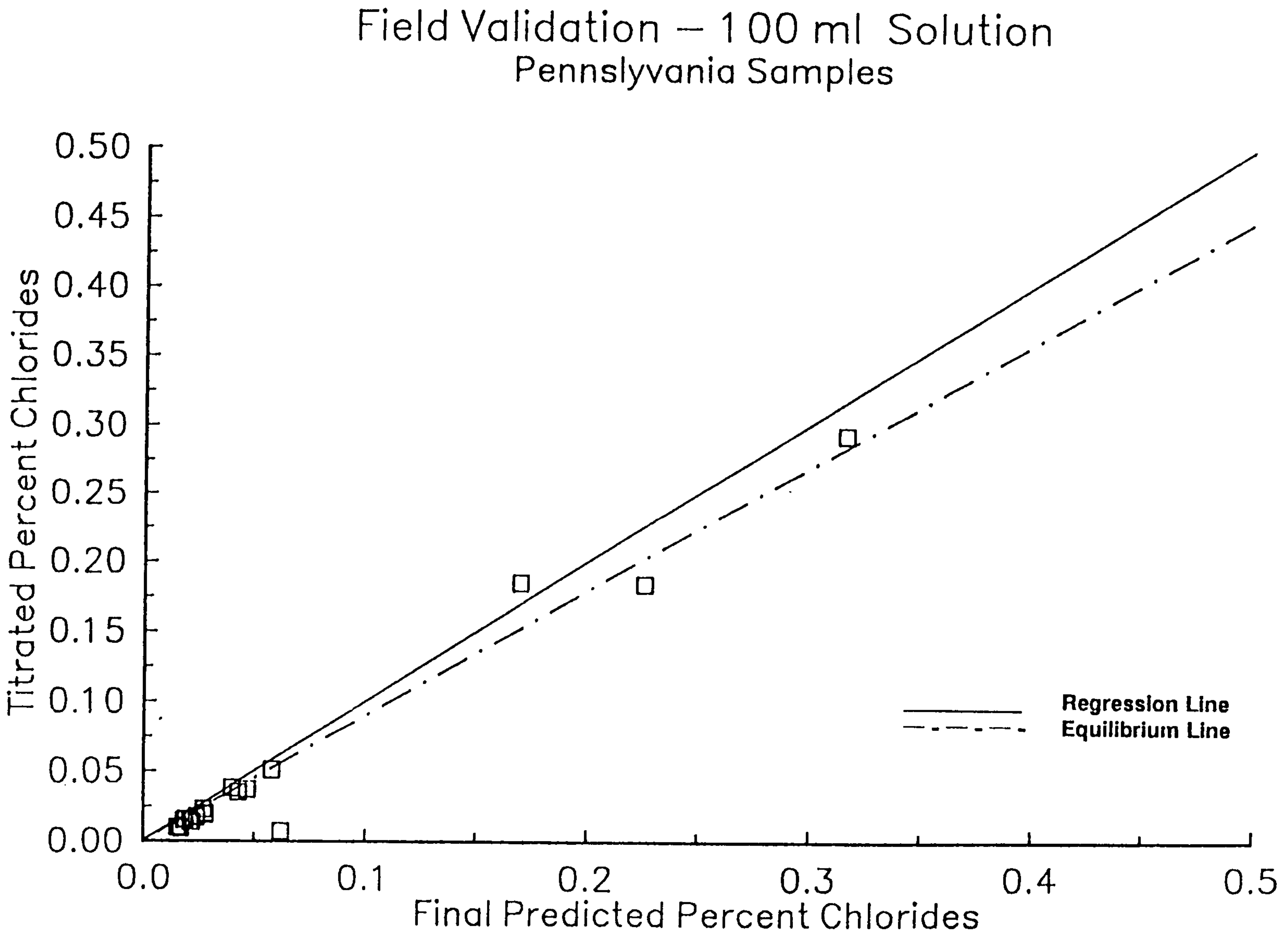


Figure 5-6. The relationship between the chloride contents using the standard and developed methods for Pennsylvania samples.

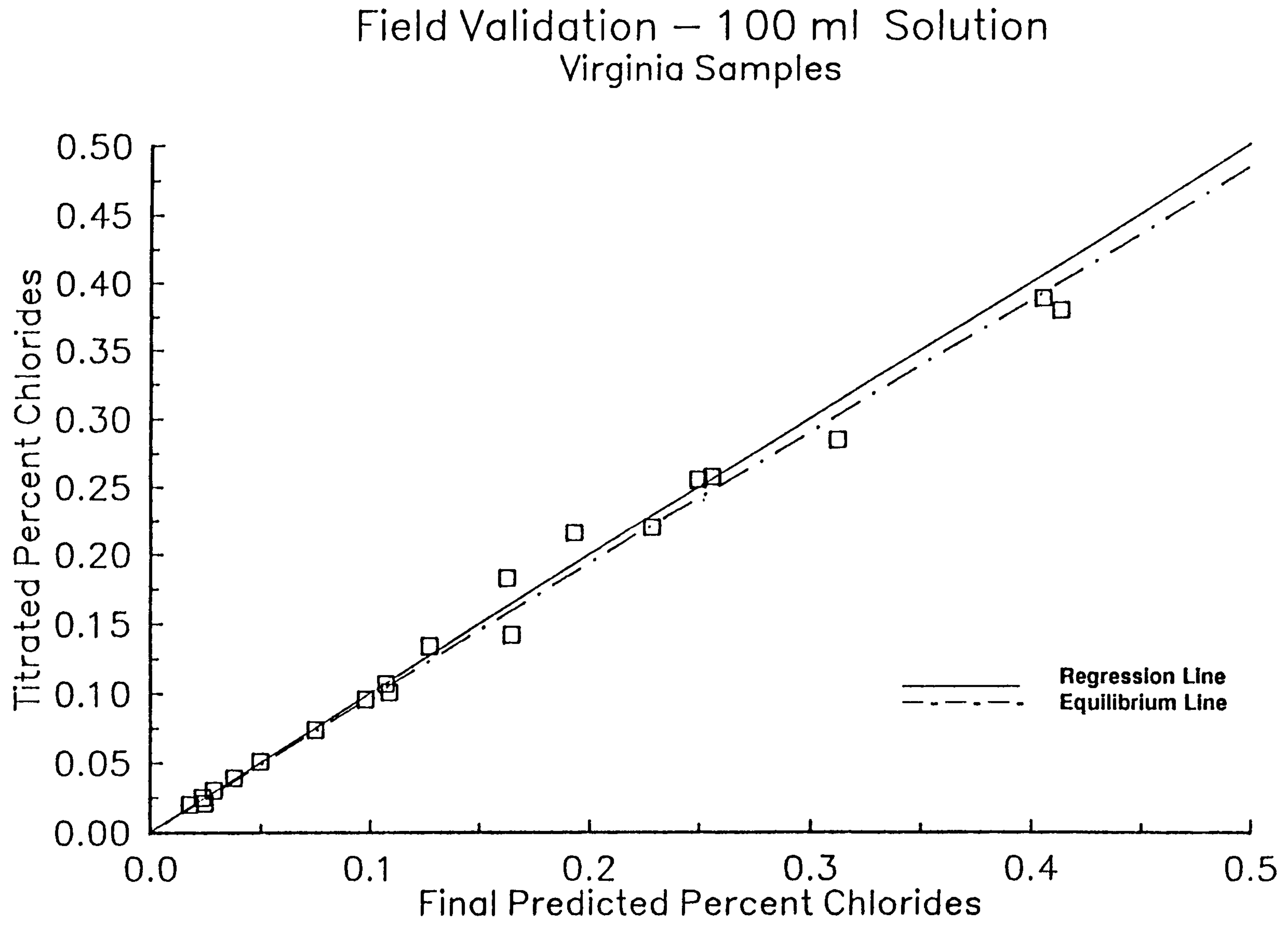


Figure 5-7. The relationship between the chloride contents using the standard and developed methods for Virginia samples.

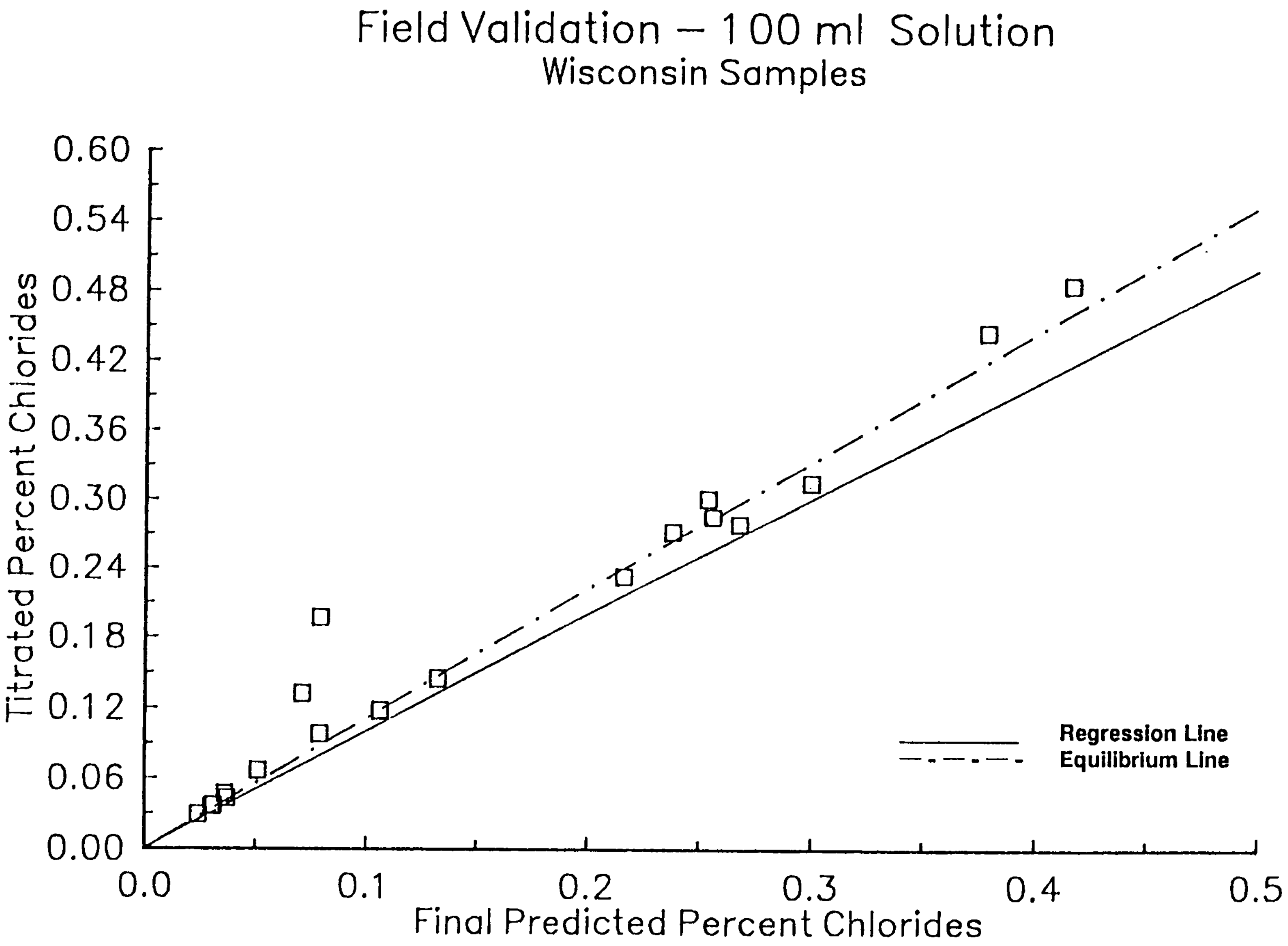


Figure 5-8. The relationship between the chloride contents using the standard and developed methods for Wisconsin samples.

Combined State Samples

The results from the four States were combined and the following equation was obtained:

$$(\%\mathrm{Cl})_{\mathrm{standard}} = + 1.03\ (\%\mathrm{Cl})_{\mathrm{measured}} \qquad (5\text{-}10)$$

The regression results are presented in Figure 5-9.

The regression models presented above indicate a very strong correlation between the standard and the developed methods for measuring chloride content.

Operator Variance

To determine the effects of different operators when using the revised procedures, 20 samples from each of the 4 previously mentioned states were analyzed by 2 operators. The results of the test are summarized in Tables 5-11 through 5-14, containing the millivolt readings and final percent chloride.

In comparing the two operators (Figure 5-10), a strong correlation was observed between the operators' results (correlation coefficient = 92.3 percent). The following statistical analysis was performed to verify the correlation.

Source	DF	MS	F_c Value	P	F_b Value
Operator	1	0.02778	1.09	0.298	3.84
State	3	0.35457	1.389	0.000	2.60
Operator*State	3	0.02009	0.79	0.503	2.60
Error	152	0.02552			
Total	159				

Hypothesis: $\mu_1 = \mu_2$
Alternative: $\mu_1 \neq \mu_2$

Using the above hypothesis (means are equal), the calculated F values (F_c) failed to exceed critical values (F_b). Thus, there are no significant differences between mean values for the two operators nor for the Operator*State interactions.

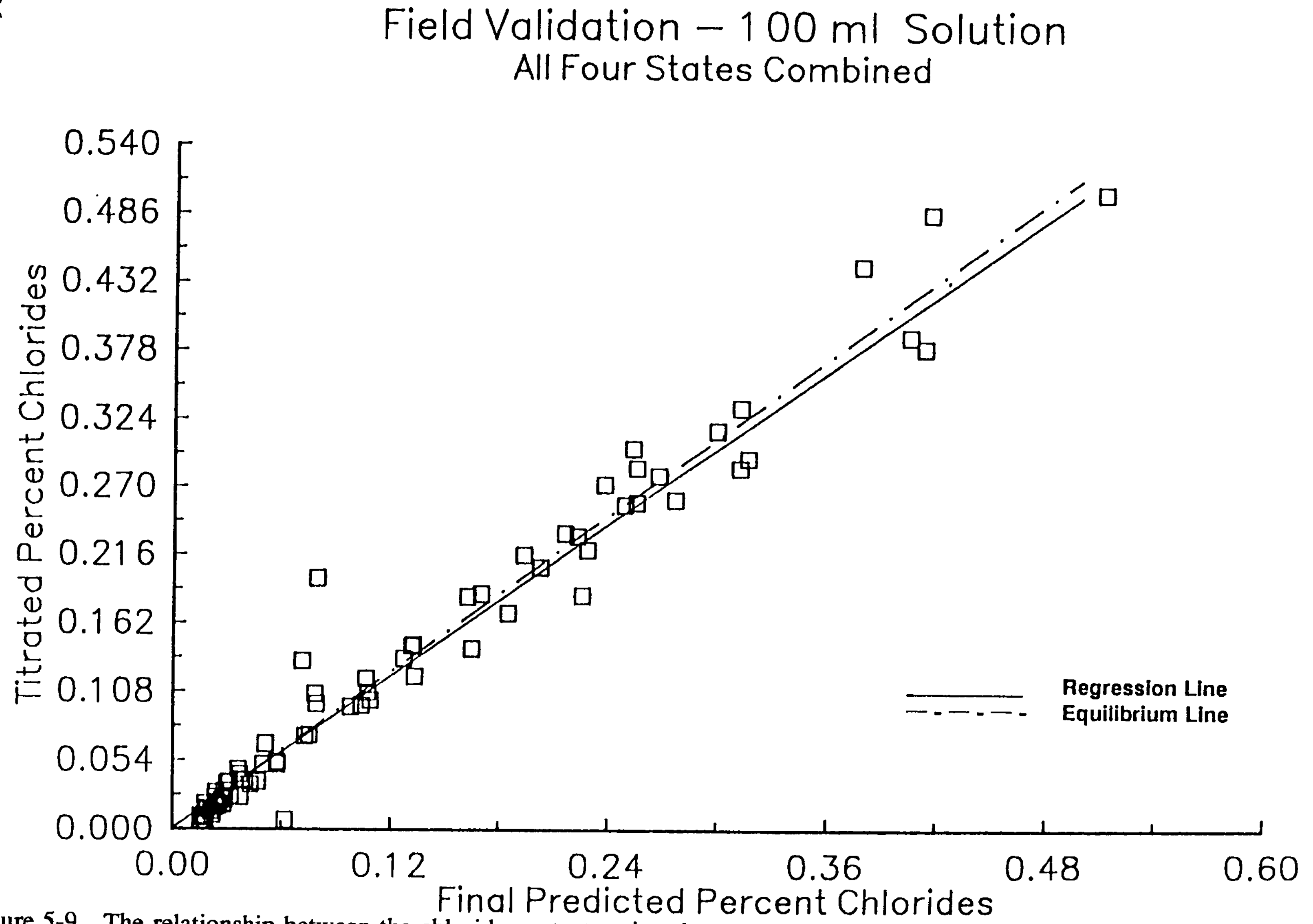


Figure 5-9. The relationship between the chloride contents using the standard and developed methods for the combined state samples.

Table 5-11. Operator variance data for Florida samples.

	Operator 1		Operator 2	
Sample	Millivolt Reading	Predicted %Cl	Millivolt Reading	Predicted %Cl
DC-5	82.8	0.017	81.5	0.017
PC1-3	19.8	0.490	23.5	0.382
PO2-2	63.3	0.034	65.8	0.030
B2-5	94.5	0.013	87.4	0.015
P5-2	18.2	0.545	19.1	0.513
DD-2	71.3	0.024	72.8	0.023
B1-5(206)	94.5	0.013	92.5	0.014
DA-1	70.3	0.025	68.8	0.027
B1-5(312)	92.8	0.013	93.1	0.013
P3-6	82.1	0.017	80.8	0.017
B1A-5	94.7	0.013	88.3	0.015
C1A-2	70.5	0.025	68.0	0.028
DA-2	80.5	0.018	78.5	0.019
C1-4	77.3	0.019	73.2	0.022
P3-3	54.7	0.054	50.7	0.067
P1-5	95.2	0.013	66.3	0.030
C1-2	91.8	0.014	88.0	0.015
C6-6	95.8	0.013	89.7	0.014
C5-5	95.9	0.013	88.9	0.014
C2-2	92.3	0.014	88.8	0.014

Table 5-12. Operator variance data for Pennsylvania samples.

Sample	Operator 1		Operator 2	
	Millivolt Reading	Predicted %Cl	Millivolt Reading	Predicted %Cl
C1-3	70.5	0.025	80.8	0.017
D-1	25.3	0.338	31.8	0.220
E-2	59.4	0.042	69.8	0.026
P1-3	50.1	0.070	58.8	0.043
D-3(11/15)	67.5	0.028	79.5	0.018
H-2	53.3	0.058	57.9	0.045
P2-1	24.5	0.357	26.2	0.319
A-2	52.1	0.062	53.6	0.057
A-4	78.7	0.019	80.9	0.017
K-4	64.5	0.032	70.3	0.025
C2-2	67.1	0.029	66.5	0.029
D-3(I80)	80.4	0.018	79.9	0.018
K-2	69.4	0.026	77.5	0.019
E-4	73.4	0.022	75.8	0.020
I-2	64.1	0.033	75.8	0.020
B-3	47.9	0.079	50.1	0.070
L-2	57.4	0.046	69.9	0.025
I-1	28.9	0.266	28.8	0.268
A-3	70.5	0.025	78.8	0.019
H-2	53.3	0.058	38.8	0.140

Table 5-13. Operator variance data for Virginia samples.

	Operator 1		Operator 2	
Sample	Millivolt Reading	Predicted %Cl	Millivolt Reading	Predicted %Cl
B1-4	66.3	0.030	65.2	0.031
C-3(927)	38.3	0.144	35.7	0.171
G-4	84.4	0.016	71.8	0.024
P2-3	66.1	0.030	51.8	0.063
B-4	42.2	0.113	43.5	0.104
D-5	42.8	0.109	39.6	0.133
C-3(676)	57.1	0.047	58.6	0.043
E-2	35.0	0.178	34.8	0.181
F-3	73.4	0.022	71.2	0.024
F-2	36.3	0.164	29.4	0.258
G-1(927)	19.9	0.486	25.8	0.327
G-1(670)	35.6	0.172	33.7	0.194
B1-2	29.4	0.258	27.5	0.292
G-2	30.7	0.236	33.2	0.201
P1-2	42.7	0.109	46.2	0.088
A-2	23.5	0.382	19.0	0.517
L-1	32.5	0.210	37.4	0.153
D-2(670)	37.1	0.156	36.0	0.167
L-3	66.3	0.030	67.9	0.028
D-2(676)	25.7	0.329	27.7	0.288

Table 5-14. Operator variance data for Wisconsin samples.

Sample	Operator 1 Millivolt Reading	Operator 1 Predicted %Cl	Operator 2 Millivolt Reading	Operator 2 Predicted %Cl
B-5	51.1	0.066	48.8	0.075
A-5	35.5	0.173	46.2	0.088
C-3	36.1	0.166	37.4	0.153
A2-3	56.6	0.048	67.5	0.028
K-1	14.6	0.696	18.3	0.542
B-2	34.5	0.184	25.8	0.327
F-1	21.9	0.425	26.9	0.304
L-2	19.7	0.493	31.9	0.219
K-3	30.6	0.238	35.8	0.169
G-3	18.5	0.534	26.7	0.308
D-5	44.1	0.100	44.5	0.098
B-6	52.2	0.062	56.3	0.049
F-5	55.3	0.052	62.5	0.036
D-3	31.5	0.224	34.4	0.186
E-2	20.3	0.473	19.0	0.517
A-3	18.5	0.534	27.7	0.288
C-6	58.1	0.044	57.5	0.046
I-5	52.1	0.062	61.0	0.038

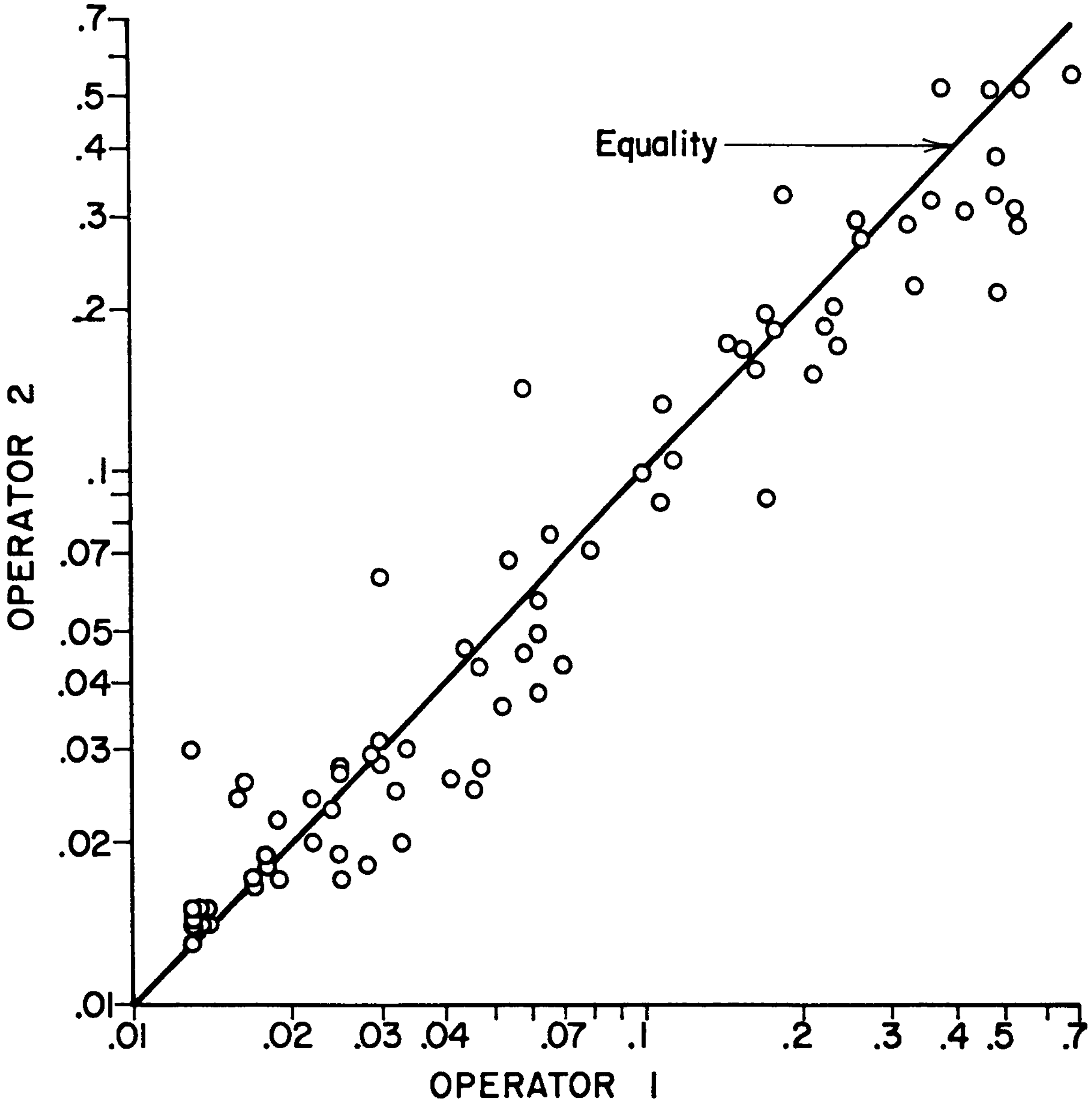


Figure 5-10. Comparison of the chloride content determinations by two operators on concrete specimens from four states.

6

Summary and Recommendations

An alternative method to the standard AASHTO test method T260-78 was developed to determine the chloride content in reinforced concrete structures. The developed method introduces a new test procedure and a newly developed digestion solution. The procedure also reduces the time per measurement dramatically compared to the AASHTO method, thus covering more area in a work day. The specific ion probe in combination with a potentiometer can accurately determine the chloride contents of concrete samples. The following points summarize the findings and recommendations from this research:

- Specific ion probe test results are not affected by different cement contents, but are affected by changes in temperature.

- Field validation indicated a good relationship between the results obtained using the specific ion probe and the results obtained using the standard potentiometric titration procedure. Also, the procedure developed for the specific ion probe required 5 to 6 minutes to analyze a concrete specimen in the field. Therefore, under field conditions, 40 to 50 specimens can be analyzed during an 8-hour work shift. Using the same procedure, 70 to 80 specimens can be analyzed in the laboratory in an 8-hour shift.

- The volumetric method for sample preparation was replaced by weighing. Variance in the results based on the plastic vials was noticed and can be linked directly to the method of placing the concrete powder into the vials. It is difficult to compact the powder into the vial and achieve the same compaction each time. Among the three weighing methods used, the triple beam balance was chosen. The triple beam balance operates very smoothly and produced a mean of 3.04 g and a standard deviation of 0.050 g.

- In the selection of the instrumentation, the only variability pertains to the potentiometer, since the specific ion probe has only one manufacturer. Therefore, the meter has to contain an accurate millivolt scale, with tenths, and be durable.

- A non-chlorine based digestion solution containing a chemical to reduce the effervescence created from limestone aggregates was developed. Accuracy of the analysis was improved by increasing the digestion solution to a volume of 20 ml. Eighty ml of a stabilizing solution was added following digestion of the concrete sample for both dilution and temperature reduction. The dilution improved the accuracy of the readings with high chloride contents, while also reducing the solution temperature below the critical 5°F (3°C) differential above ambient. Thus the use of the stabilizing solution eliminates the problem of erroneous determinations due to temperature variations, a problem that the research revealed to be unamenable to solution by calibration procedures.

- A rapid, efficient, low-cost means of acquiring powdered concrete samples in the field was developed in this research.

- It was shown that a sufficiently significant relationship exists between chloride contents determined on samples that were crushed to pass the No. 50 (300 μm) sieve size and those that were not to obviate the need for crushing.

- It was found that variable cement contents in the concrete samples do not have a significant effect on chloride content determinations.

- The calibration solution range was increased for improved interpretation at higher chloride concentrations. The new solution range covers the probable range encountered in the field.

- Results with standard solutions were repeatable for a specified potentiometer and probe combination. However, periodic measurements should be performed using the calibration solutions to ensure proper operation. Different meter-probe combinations produced independent intermediate values, but final analysis rendered similar results. To ensure no misinterpretations, meters and probes should be calibrated and held in a permanent configuration for the lifetime of the instruments.

- In the presence of concrete, the specific ion probe reacts differently than in pure saline solutions. The concrete residue forces the chloride interpretation to be adjusted for comparisons with the AASHTO method T260-84. Once adjusted, the specific ion probe accurately determines the chloride content of concrete. Results based on samples from the field indicated that the revised procedures developed in this research produce strong correlations with AASHTO T260 for the lower concentrations and increased accuracy for the higher ranges.

- Strong correlation was observed between the individual analyzed States: Florida, Wisconsin, Pennsylvania, and Virginia. Each state contained separate aggregate sources, yet the results were comparable to the AASHTO method. Therefore, the probe's only restrictions are those specified by the manufacturer.

- The operator variance was studied. The results indicated that various operators would produce similar results. Since the instruments require minimal technical skills, the procedure could be performed at any analytical level and still maintain similar results.

A test procedure, in ASTM format, for determining chloride contents of powdered concrete samples based on this research has been prepared and can be found in Volume 8, "Procedure Manual" of this report series.

Appendix A

Chloride Analysis Procedures

The Standard Potentiometric Titration, AASHTO T260-84

This method was used as the basis for comparison of the chloride content of the test samples. The following procedure was used. Three g of the powdered concrete sample are weighed to the nearest mg. Ten ml of 90 to 100°C distilled water are added and the sample is swirled. After the sample is in suspension, the slurry is ground to remove any lumps and then transferred into a beaker. Three ml of concentrated nitric acid are added to the remaining sample material, and this mixture is transferred quantitatively into the beaker while the slurry is stirred constantly. The solution is increased to approximately 50 ml by adding hot distilled water.

Five drops of methyl orange indicator are added to the slurry, and the pH of the sample is adjusted if needed. The solution is then covered with a watch glass and the stirring rod is left in the beaker. Next, the solution is heated, allowed to boil for 1 minute, and then removed from the heat. The sample is filtered into another beaker and the beaker, filter paper, funnel, and stirring rod are rinsed thoroughly to ensure complete transfer of the chloride. Finally, the sample is allowed to cool to room temperature.

Four ml of 0.01N NaCl solution are added to the sample prior to titration with 0.01N $AgNO_3$ solution. A chloride specific electrode, Orion Model 94-17B, its reference electrode, and a millivoltmeter are used in the determination of the titration end-point.

James Instruments, Model Cl 500

The procedure used for testing the chloride content of concrete specimens is as follows:

1. Calibration of the electrometer: Turn the electrometer on and set the dial to read V (volts). Insert the specific ion electrode into one of the standard solutions supplied with the instrument. Allow the electrometer reading (mV) to stabilize by waiting approximately 1 1/2 to 2 minutes. Record the readings and the number corresponding to the standard solution. Repeat for the two remaining standard solutions. Calibration of the electrometer should be done each time the instrument is turned on.

2. Analysis of powdered concrete samples: Prior to weighing, stir the powdered sample thoroughly to ensure a uniform mixture of chloride-contaminated concrete powder. Weigh 3.0 g of the powdered sample to the nearest 0.1 mg using an analytical balance. Place the 3.0-g sample into the supplied chloride extraction liquid and shake for 15 seconds Insert the electrode into the digested sample for 3 minutes and record the mV reading.

3. Modifications of the original procedure suggested by James Instruments *(21)* included weighing each specimen using a precision balance and increasing the time before reading the results on the electrometer to a minimum of 3 minutes. After the 3 minutes, if the change in the mV reading resulted before the reading was recorded, the new reading was adopted. The specific ion probe used during this investigation is shown in Figure A-1.

4. The calibration procedure:

    - Turn the dial on the electrometer to read V (volts); corresponding readings will result in mV.

    - Do not allow the electrometer battery to become weak. Erratic readings may result.

    - Refrain from storing the calibration liquids in direct sunlight or in very warm places.

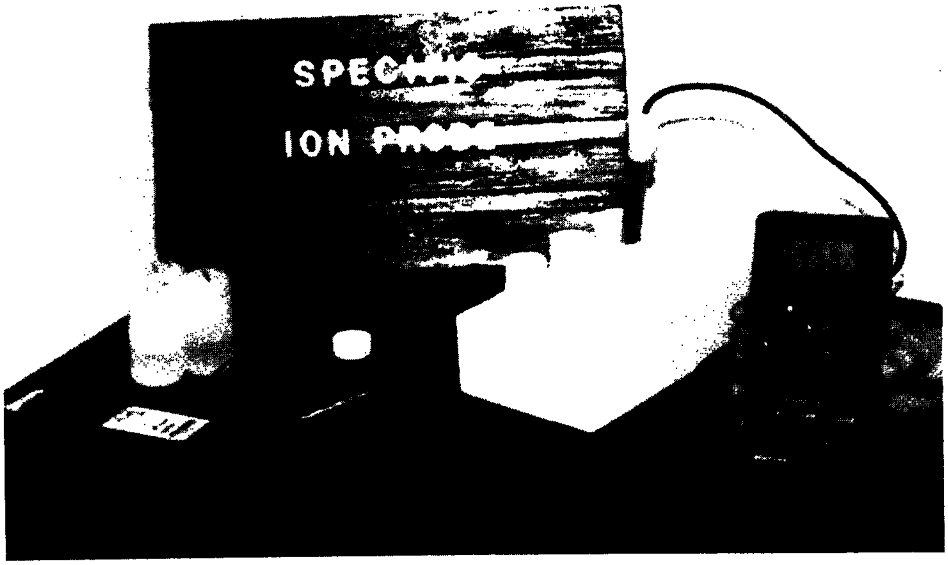


Figure A-1. The specific ion probe.

- Care should be taken to prevent contamination of the three calibration liquids. An extreme increase or decrease in the mV readings may indicate contamination of one or more of the liquids. Normally, calibration readings should be within ± 5 mV of previous readings and approximately 100 mV, 50 mV, and -5 mV for calibration liquids 1, 2, and 3, respectively.

- Ensure that the distilled water does not become contaminated. Also, it is recommended that only salt-free distilled water is used.

- Special care of the electrode is important. When not in use, the electrode should be submerged in distilled water to prevent clogging of the sensing device.

- If the filling solution is allowed to remain in the electrode for extended periods of time, damage to the electrode may result. Clean and polish the electrode frequently to maintain consistent results.

- Prior to using the electrode, observe the level of the filling solution. An insufficient amount of filling solution will result in readings that wander and reduce the repeatability of the results. Variable readings were noticed after the level fell below 1/4 in. of the eyelet in the probe. For best results, it is recommended that the probe be filled completely with filling solution prior to use.

- The specific ion probe should be cleaned using distilled water only.

- Never touch the tip of the probe.

- Polish the tip of the probe using the polishing strip provided by the manufacturer at frequent intervals, depending on the amount of use.

Spectrophotometer, Hach DR/2000

1. Sample preparation: Prior to weighing, stir the powdered sample thoroughly to ensure a uniform mixture of chloride. Weigh 1.0 g of the powdered sample to the nearest 0.1 mg using an analytical balance. Place the sample in a 250-ml beaker. Add approximately 5 to 10 ml of deionized water. Next, add 5 ml of concentrated nitric acid and stir vigorously for 10 seconds After fizzing settles,

transfer the sample to a second 250-ml beaker using a filtering apparatus and Whatman 40 filter paper. When filtering, rinse the sample in the filter 4 to 5 times to ensure a complete transfer of the chloride. Rinse the outer lip of the beaker. After filtering, rinse the outside of the filter paper 3 to 4 times and rinse the funnel and funnel tip thoroughly, allowing all of the filtrate to be transferred into the sample beaker. If a precipitate exists, refilter the sample using the above procedure. After filtering, increase the sample volume to 100 ml using a graduated cylinder and distilled water. Transfer the sample in the graduated cylinder back into the same 250-ml beaker.

2. Filtrate analysis: Specify the chloride test procedure on the spectrophotometer by pressing 7 0 ENTER. Enter the appropriate wavelength reading (455) for the chloride test. Two sample cells are prepared, one with deionized water and the other with the filtered sample to be analyzed. Pipet 25 ml of the sample into one of the same cells. Next, pipet 25 ml of deionized water into the matching sample cell. Add 2 ml of mercuric thiocyanate to each sample cell. Next, add 1 ml of ferric ion solution to each sample and swirl to mix. Observe the samples to determine if any interferences that may reduce the accuracy are present. Press SHIFT TIME on the instrument; a 2-minute time period will start. During this waiting period, wipe the outside of the sample cells to remove any dirt or spots. After the 2-minute period, place the sample cell containing no chloride into the slot provided in the instrument with the numbers on the cell facing to the left. Press zero on the instrument. After the instrument provides a reading of 0 mg/l, remove the blank cell and place the cell containing the chloride sample into the instrument in a similar manner. Press READ, wait, and record the results.

3. Modifications of the original procedure suggested by the Hach Company (22) involved the preparation of the sample prior to testing. The procedure developed by the Hach Company was applicable to water samples. Therefore, a procedure for extracting the chloride from the powdered concrete specimens was developed prior to analyzing the samples using the procedure recommended by the Hach Company for analyzing the chloride content of water.

   The spectrophotometer was developed mainly for detecting low levels of chloride. In addition, this procedure is very sensitive to interferences resulting from low pH or acidic samples. Therefore, a 1.0-g sample was weighed and acid-digested using .5 ml concentrated nitric acid. After the filtering process, the prepared sample of 100 ml was consistently above a pH of 3. Twenty-five ml of this sample were analyzed for chloride content. As a result, no interferences were detected throughout the testing procedure. The spectrophotometer used in this study is shown in Figure A-2.

CD-DT Digital Titrator (Hach Company)

The same sample procedure used with the spectrophotometer method is adopted for the CD-DT digital titrator method.

1. Filtrate analysis: Remove 25 ml of the sample in the 250-ml beaker using a pipet. The sample now contains 75 ml. Place the 75-ml sample on a magnetic stirrer and insert a magnetic stirring rod. Using a pH probe, adjust the pH of the sample using perchloric acid (1:5 dilution) to 2.5 ± 0.1. If necessary, sodium hydroxide (5N) may be used to adjust the pH upward. After the pH is properly adjusted, add the contents from one of the chloride2 powder pillows while stirring. The sample will turn from a clear to a bright yellow color. Next, insert one of the 1.128N silver chloride containers into the digital titrator. Insert one of the titrating tubes into the tip of the silver chloride. Turn the dial until the silver chloride drips from the end of the red tube. Using a chemical-free tissue, wipe the end of the tip to remove any silver chloride from the outside. Zero the dial on the digital titrator and insert the red tip into the 75-ml sample. Turn the dial to titrate the sample. Observe the first consistent color change, reddish yellow or brownish yellow, which indicates the midpoint of the titration. Read and record the number of digits required for titrating the sample.

2. Modification of the original procedure suggested by the Hach Company (*26*) involved the preparation of the sample prior to testing. The procedure developed by the Hach Company was applicable to water samples. Consequently, a procedure for extracting the chloride from the powdered concrete specimens was developed prior to analyzing the samples using the procedure recommended by the Hach Company for analyzing the chloride content of water.

   Unlike the spectrophotometer, the digital titrator was developed for detecting higher levels of chloride. This procedure is also sensitive to interferences resulting from pH. Therefore, a 1.0-g sample was weighed and acid-digested using .5 ml concentrated nitric acid. After the filtering process, the prepared sample of 100 ml was consistently above a pH of 3. Seventy-five ml of this sample were analyzed for chloride content. Prior to the analysis, each sample was adjusted to a pH ranging from 2.4 to 2.6. As a result, no interferences were

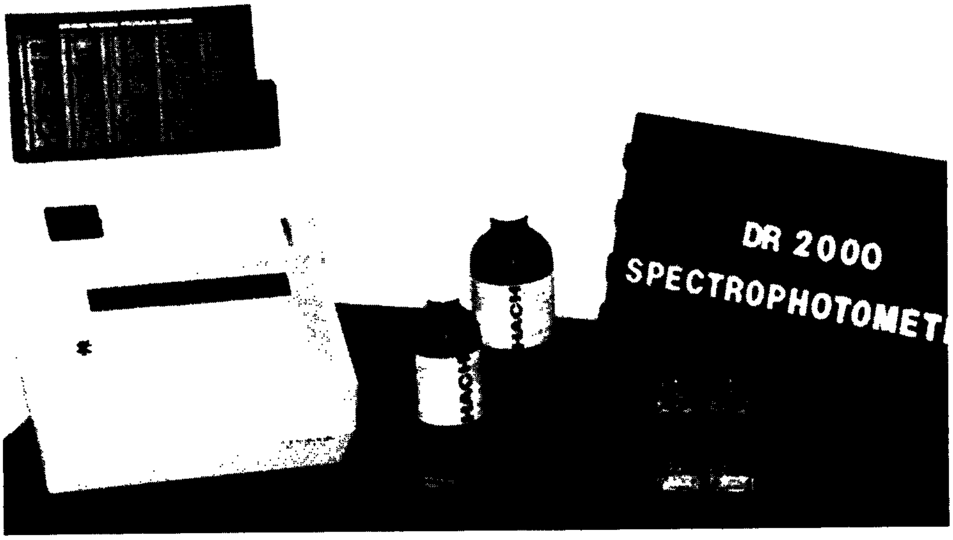


Figure A-2. The DR 2000 spectrophotometer.

detected throughout the testing procedure. The digital titrator used during the investigation is shown in Figure A-3.

Quantab Titrator Strips (Standard)

1. Powdered concrete sample preparation: Prior to weighing, stir the powdered sample thoroughly to ensure a uniform mixture of chloride. Weigh 10.0 g of the powdered sample to the nearest .1 mg using a precision scale. Place the sample in a 250-ml beaker. Add 90 ml of boiling distilled water, stirring constantly. Stir the sample for 30 seconds, and, after 1 minute, stir the sample again for another 30 seconds. Fold Whatman 40 filter paper twice, into a cone, and place it into the beaker. Allow some of the sample to filter through.

2. Chloride analysis procedure: Place a Quantab titrator strip in the filtered portion of the sample and allow it to remain until a dark blue color forms at the top of the strip. Allow 5 to 10 minutes for the color to change. Read the Quantab titrator strip to the nearest .05 mark at the uppermost point of the color change. This color may be white or yellowish orange. Record the readings.

3. Modified Quantab titrator strips: The procedure developed by Environmental Test Systems, Inc. (*27*) was used initially for analyzing the chloride content of the test specimens. This procedure provided an analysis of the water-soluble chloride present in the specimens. Because background chloride is also present in concrete bridge components, the procedure was modified to provide for an acid digestion of the sample prior to testing. Ten g of the powdered samples were weighed, followed by the addition of 3 ml of nitric acid. The volume of the sample was increased to 100 ml. Then, the sample was tested for chloride content using the Quantab titrator strip. Prior to testing each sample, a pin hole was inserted along the yellow line near the top of the strip as recommended by Environmental Test Systems, Inc. (*26*) to obtain more accurate results.

   The modified procedure is as follows. Prior to weighing, stir the powdered sample thoroughly to ensure a uniform mixture of chloride. Weigh 10.0 g of the powdered sample to the nearest .1 mg using an analytical balance. Place the sample in a 250-ml beaker. Add approximately 5 to 10 ml of distilled deionized water. Next, add 3 ml of concentrated nitric acid. Stir vigorously for 15 seconds. Wait 1 minute and stir again for 15 seconds. After the fizzing

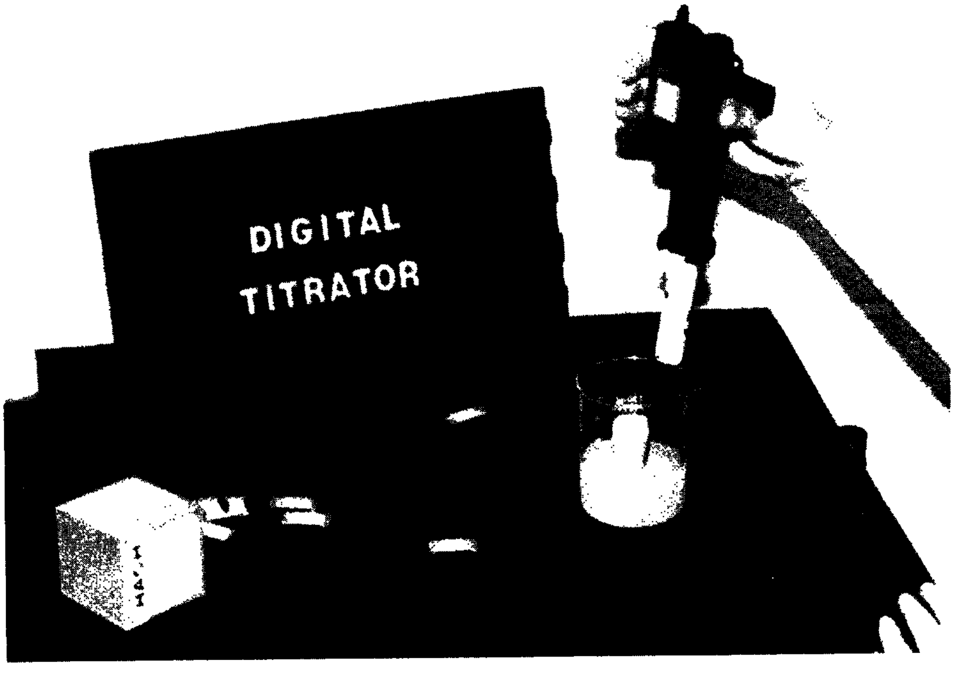


Figure A-3. The digital titrator.

settles, fold the filter paper (Whatman 40) twice to form a cone. Place the filter paper into the beaker containing the sample. Allow some filtrate to filter into the cone. Using a stick pin, punch a hole in the top of the strip along the yellow line. Place the Quantab titrator strip in the filtered portion of the sample and allow it to remain until a dark blue color forms at the top of the strip. Allow 5 to 10 minutes for this to occur. Read the Quantab titrator strip to the nearest .05 mark at the uppermost portion of the white color change. Notice that this portion may not extend across the entire Quantab strip. Record the reading.

The Quantab titrator strips used during this study are shown in Figure A-4.

Figure A-4. The Quantab titrator strips.

Appendix B

Chloride Content Results for Bridges in Field Validation Study

Table B-1. Predicted chloride content values for Pennsylvania bridge PA 180 over 220 WB.

	Specific Ion Probe*			Potentiometric Titration Predicted Values*	
Sample Number	Reading (M-Volts)	Reaction Temperature (°F)	Calculated Chloride ($\%Cl^-$)	($\%Cl^-$)	(lb/cu yd)
A-1	27.8	66	.112	.07	2.68
2	59.3	71	.028	.02	.72
3	81.6	70	.008	.01	.26
4	108.5	69	0	0	.00
B-1**	3.5	72	.336	.30	11.66
2**	10.9	70	.242	.17	6.80
3**	34.2	70	.087	.05	2.05
4**	56.4	72	.033	.02	.83
C-1	-1.3	75	.388	.40	15.81
2	11.3	76	.228	.16	6.25
3	38.3	80	.076	.05	1.80
4	63.2	78	.027	.02	.71
D-1	1.5	65	.308	.25	9.93
2	26.6	64	.102	.06	2.42
3	44.6	65	.045	.03	1.10
4	73	61	.006	.00	.19
E-1	56.7	68	.026	.02	.75
2	99.7	64	0	.00	.00
3	104.9	64	0	.00	.00
4	LOST	LOST	LOST	LOST	LOST
F-1	25.1	68	.113	.07	2.70
2	62	65	.018	.01	.50
3	84.9	64	.012	.01	.35
4	107.5	68	0	.00	.00
G-1	19	79	.174	.11	4.40
2	52.1	80	.046	.03	1.12
3	80	84	.019	.01	.52
4	94.9	75	.007	.01	.22
H-1	5.7	76	.302	.24	9.63
2	37.7	70	.074	.04	1.76
3	60.6	74	.029	.02	.74
4	105.6	82	.009	.01	.28

Table B-1. (*continued*)

	Specific Ion Probe*			Potentiometric Titration	
		Reaction	Calculated	Predicted Values	
Sample Number	Reading (M-Volts)	Temperature (°F)	Chloride (%Cl$^-$)	(%Cl$^-$)	(lb/cu yd)*
I-1	6.9	77	.288	.23	8.88
2	30.7	74	.104	.06	2.47
3	69.9	75	.020	.01	.54
4	93.3	76	.008	.01	.26
J-1	17.9	79	.180	.12	4.59
2	59.7	80	.034	.02	.87
3	88	80	.013	.01	.37
4	103.6	83	.010	.01	.31
K-1	LOST	LOST	LOST	LOST	LOST
2	87.1	75	.020	.01	.53
3	97.7	81	.010	.01	.31
4	111.9	83	.009	.01	.27
L-1	25.8	82	.132	.08	3.20
2	91.1	83	.014	.01	.39
3	116.6	89	.012	.01	.36
4	111.8	83	.009	.01	.28

* Samples were crushed to minus 50 mesh

** Actual sample numbers were:

B-1** => B-4 depth 1$^{3}/_{4}$" to 2$^{1}/_{4}$"
B-2** => B-1 depth $^{1}/_{4}$" to $^{3}/_{4}$"
B-3** => B-2 depth $^{3}/_{4}$" to 1$^{1}/_{4}$"
B-4** => B-3 depth 1$^{1}/_{4}$" to 1$^{3}/_{4}$"

Table B-2. Predicted chloride content values for Pennsylvania bridge PA 180 over 220 EB.

	Specific Ion Probe			Potentiometric Titration Predicted Values	
Sample Number	Reading (M-Volts)	Reaction Temperature (°F)	Calculated Chloride (%Cl^-)	(%Cl^-)	(lb/cu yd)
A-1	25.2	83	.133	.093	3.67
2	31.5	81	.102	.074	2.91
3	85.8	83	.016	.009	.37
4	94.6	82	.012	.006	.23
B-1	6	81	.288	.180	7.11
2	26.1	83	.128	.090	3.55
3	62.9	81	.031	.023	.89
4	86.5	82	.015	.009	.34
C-1	11.9	81	.226	.147	5.80
2	LOST	LOST	LOST	LOST	LOST
3	LOST	LOST	LOST	LOST	LOST
4	LOST	LOST	LOST	LOST	LOST
D-1	50.2	82	.050	.038	1.48
2	89.6	84	.015	.009	.34
3	96.6	85	.013	.007	.28
4	110.3	81	.008	.002	.06
G-1	7.7	84	.270	.171	6.75
2	54.4	85	.044	.034	1.32
3	77.5	85	.021	.014	.57
4	94.4	83	.013	.006	.26
H-1	6.9	82	.272	.172	6.78
2	49.3	84	.051	.038	1.51
3	84.5	85	.017	.011	.42
4	100.9	84	.011	.005	.20
I-1	9.4	86	.248	.159	6.27
2	49	85	.052	.039	1.55
3	91.3	85	.014	.008	.32
4	108.5	86	.011	.005	.20

Table B-3. Predicted chloride content values for Pennsylvania bridge PA 11-15 over 35 NB.

	Specific Ion Probe			Potentiometric Titration Predicted Values	
Sample Number	Reading (M-Volts)	Reaction Temperature (°F)	Calculated Chloride (%Cl^-)	(%Cl^-)	(lb/cu yd)
A-1	35.9	86	.088	.064	2.54
2	85.9	89	.019	.013	.50
3	85.3	86	.018	.011	.44
4	76.7	85	.021	.015	.58
B-1	33.3	88	.099	.071	2.82
2	62.3	87	.035	.026	1.02
3	94.5	88	.016	.009	.37
4	100.5	87	.013	.007	.29
C-1	37.6	85	.082	.060	2.38
2	70.8	86	.026	.019	.74
3	106.4	88	.013	.007	.27
4	95.6	88	.015	.009	.36
G-1	40.4	84	.073	.054	2.14
2	92.5	87	.016	.009	.37
3	81.2	89	.021	.015	.58
4	87.5	85	.016	.010	.39
H-1	12.7	83	.219	.143	5.64
2	27.6	85	.121	.086	3.38
3	60	85	.036	.027	1.07
4	78	84	.020	.013	.53
I-1	16	84	.192	.128	5.05
2	64.2	86	.032	.024	.94
3	77.7	85	.021	.014	.56
4	86.1	85	.017	.010	.41
P1-1	-23.1	81	.961	.488	19.23
2	-7.5	86	.505	.288	11.35
3	26.7	84	.125	.088	3.47
4	81.6	81	.016	.010	.39
5	90	83	.014	.008	.30

Table B-3. (*continued*)

	Specific Ion Probe			Potentiometric Titration Predicted Values	
Sample Number	Reading (M-Volts)	Reaction Temperature (°F)	Calculated Chloride (%Cl$^-$)	(%Cl$^-$)	(lb/cu yd)
P2-1	2.4	80	.332	.203	8.02
2	54.8	83	.042	.032	1.25
3	84.2	84	.017	.010	.41
4	88.7	82	.014	.008	.30
C1-1	60	83	.035	.026	1.02
2	70.6	84	.025	.018	.70
3	71	82	.023	.016	.65
4	90.4	86	.016	.009	.37
C2-1	51.2	85	.049	.037	1.46
2	57.2	85	.040	.030	1.18
3	62.5	83	.032	.024	.93
4	81.6	83	.017	.011	.43

Table B-4. Predicted chloride content values for Pennsylvania bridge PA 11-15 over 35 SB.

	Specific Ion Probe			Potentiometric Titration Predicted Values	
Sample Number	Reading (M-Volts)	Reaction Temperature (°F)	Calculated Chloride (%Cl^-)	(%Cl^-)	(lb/cu yd)
A-1	30.8	71	.086	.063	2.50
2	29.6	80	.097	.070	2.78
3	57.9	79	.031	.023	.91
4	78.2	78	.014	.008	.32
B-1	-4.7	80	.401	.238	9.38
2	15.8	83	.173	.117	4.62
3	39.6	83	.067	.050	1.97
4	71.6	84	.022	.015	.60
C-1	11.3	83	.208	.137	5.40
2	49.4	80	.044	.033	1.31
3	84.1	82	.014	.008	.32
4	85.7	79	.012	.006	.22
D-1	3	81	.291	.182	7.19
2	41.3	79	.060	.045	1.78
3	80.8	81	.015	.009	.35
4	89.1	81	.012	.006	.22
E-1	17.7	80	.158	.108	4.27
2	69.1	82	.022	.016	.62
3	93.1	80	.010	.004	.15
4	99.7	81	.009	.003	.11
F-1	44.4	80	.055	.042	1.64
2	74	80	.018	.012	.48
3	88.3	80	.012	.006	.22
4	92.7	80	.010	.004	.17

Table B-4. (*continued*)

	Specific Ion Probe			Potentiometric Titration Predicted Values	
Sample Number	Reading (M-Volts)	Reaction Temperature (°F)	Calculated Chloride (%Cl-)	(%Cl-)	(lb/cu yd)
G-1	19.3	80	.152	.105	4.13
2	41.9	82	.062	.047	1.84
3	78.5	80	.016	.010	.38
4	81.8	82	.016	.009	.37
H-1	14.7	79	.183	.123	4.84
2	47.5	82	.050	.038	1.50
3	66.4	83	.026	.019	.74
4	82	83	.016	.010	.39
I-1	35.7	81	.079	.058	2.30
2	67.8	81	.023	.016	.64
3	86.1	81	.013	.007	.26
4	93.7	85	.013	.007	.27
J-1	17.1	86	.173	.117	4.63
2	50.7	85	.046	.035	1.37
3	69	83	.023	.016	.65
4	90.2	84	.013	.007	.29
K-1	37.5	88	.078	.058	2.27
2	83	87	.018	.012	.46
3	81	82	.016	.009	.37
4	75.1	83	.019	.013	.51
L-1	12.4	85	.210	.138	5.44
2	61.5	85	.032	.023	.92
3	80.9	86	.018	.012	.47
4	74.4	83	.020	.013	.52

Table B-4. (*continued*)

	Specific Ion Probe			Potentiometric Titration Predicted Values	
Sample Number	Reading (M-Volts)	Reaction Temperature (°F)	Calculated Chloride (%Cl^-)	(%Cl^-)	(lb/cu yd)
P1-1	6.8	82	.263	.167	6.59
2	25.3	79	.120	.085	3.35
3	45	82	.055	.041	1.63
4	66.2	83	.026	.018	.73
P2-1	-8.1	83	.494	.283	11.15
2	13	80	.201	.133	5.26
3	41.6	80	.062	.046	1.82
4	63	83	.029	.021	.83
C1-1	70.5	82	.022	.015	.59
2	73.9	77	.016	.010	.39
3	79.6	78	.014	.007	.29
4	80.6	78	.013	.007	.28
C2-1	42.7	78	.058	.043	1.71
2	63.8	77	.024	.017	.67
3	76.6	77	.014	.008	.33
4	76.7	78	.015	.009	.35

Table B-5. Predicted chloride content values for Virginia bridge VA I-81 over 927 NB.

	Specific Ion Probe			Potentiometric Titration Predicted Values	
Sample Number	Reading (M-Volts)	Reaction Temperature (°F)	Calculated Chloride (%Cl^-)	(%Cl^-)	(lb/cu yd)
A-1	-2.8	96	.397	.236	9.31
2	17.6	94	.173	.117	4.62
3	61.5	95	.038	.028	1.12
4	91.6	97	.021	.014	.57
B-1	-21.1	95	.850	.441	17.40
2	-1.1	91	.367	.221	8.73
3	.1	96	.353	.214	8.43
4	17.1	94	.177	.119	4.70
5	27.3	96	.120	.085	3.36
C-1	2.1	95	.324	.200	7.86
2	5	97	.289	.181	7.15
3	17.3	98	.178	.120	4.73
4	30.9	98	.106	.076	3.01
D-1	-21.2	98	.855	.444	17.49
2	LOST	LOST	LOST	LOST	LOST
3	4.2	97	.299	.186	7.35
4	13.4	98	.207	.137	5.39
5	26.7	96	.123	.087	3.42
E-1	-9.3	95	.519	.295	11.62
2	6.1	95	.276	.174	6.86
3	39.9	96	.076	.056	2.22
4	79.2	98	.026	.019	.75
F-1	.9	97	.342	.208	8.22
2	23.1	96	.141	.098	3.86
3	63.8	97	.037	.028	1.08
4	89.4	97	.022	.015	.59
G-1	-17.7	98	.739	.394	15.52
2	8.7	97	.249	.160	6.30
3	62.6	100	.040	.030	1.18
4	89.1	97	.022	.015	.60
H-1	-8.7	96	.507	.289	11.39
2	1	95	.339	.207	8.17
3	13.6	99	.206	.136	5.37
4	25.8	101	.130	.091	3.60

Table B-5. (*continued*)

	Specific Ion Probe			Potentiometric Titration Predicted Values	
Sample Number	Reading (M-Volts)	Reaction Temperature (°F)	Calculated Chloride (%Cl⁻)	(%Cl⁻)	(lb/cu yd)
I-1	-1.5	99	.378	.227	8.94
2	11.2	98	.226	.147	5.80
3	38.4	97	.081	.059	2.34
4	68.3	97	.033	.024	.96
J-1	-15.5	100	.675	.366	14.42
2	-4.5	98	.427	.251	9.89
3	11.3	100	.226	.147	5.81
4	32.4	95	.099	.071	2.82
K-1	-7.9	100	.493	.282	11.13
2	21.3	97	.152	.105	4.12
3	57.6	99	.045	.034	1.33
4	82.5	98	.025	.018	.70
L-1	-9.5	98	.525	.298	11.73
2	7.5	100	.263	.168	6.60
3	23.6	100	.141	.098	3.86
4	50.6	101	.056	.042	1.66

Table B-5. (*continued*)

	Specific Ion Probe			Potentiometric Titration	
Sample Number	Reading (M-Volts)	Reaction Temperature (°F)	Calculated Chloride (%Cl$^-$)	Predicted Values (%Cl$^-$)	(lb/cu yd)
P1- 1	19.7	90	.167	.114	4.49
2	28.7	89	.114	.081	3.21
3	33.2	90	.095	.069	2.73
4	44.6	89	.060	.045	1.78
P2- 1	22.6	85	.145	.100	3.96
2	28.4	88	.115	.082	3.23
3	30	91	.109	.078	3.09
4	32.4	88	.097	.070	2.78
C1- 1	14	85	.211	.139	5.46
2	17.4	94	.187	.125	4.94
3	23.7	90	.141	.098	3.87
4	32.9	90	.119	.085	3.34
C2- 1	14.9	90	.206	.136	5.35
2	LOST	LOST	LOST	LOST	LOST
3	22.1	91	.152	.105	4.12
4	22.9	91	.147	.102	4.00
B1- 1	.7	88	.381	.228	9.00
2	5.1	90	.315	.195	7.68
3	9.4	90	.261	.166	6.55
4	17.3	87	.184	.123	4.86
B2- 1	-.8	93	.411	.243	9.57
2	2	91	.362	.219	8.62
3	23.2	91	.145	.100	3.96
4	18.8	91	.175	.118	4.65

Table B-6. Predicted chloride content values for Virginia bridge VA I-81 over 676 NB.

Sample Number	Specific Ion Probe Reading (M-Volts)	Reaction Temperature (°F)	Calculated Chloride (%Cl⁻)	Potentiometric Titration Predicted Values (%Cl⁻)	(lb/cu yd)
A-1	-12.8	93	.752	.399	15.74
2	-4.3	92	.518	.294	11.60
3	12.5	94	.253	.162	6.38
4	35.9	92	.096	.070	2.75
5	71.4	92	.029	.021	.83
B-1	-4.4	93	.521	.296	11.66
2	5.5	94	.341	.208	8.19
3	16	93	.218	.142	5.62
4	36.6	91	.093	.068	2.67
5	60.5	94	.041	.031	1.21
C-1	11.7	92	.260	.166	6.54
2	19	92	.191	.128	5.03
3	53.4	93	.051	.038	1.51
4	69	93	.031	.023	.91
D-1	-3.2	92	.494	.283	11.15
2	2.9	95	.381	.228	9.00
3	9.7	93	.284	.178	7.04
4	17.3	93	.206	.136	5.36
5	24.6	93	.152	.105	4.13
E-1	3.3	93	.374	.224	8.85
2	9.9	93	.282	.177	6.99
3	24.4	95	.155	.106	4.19
4	44.2	96	.072	.054	2.12
F-1	3.6	94	.369	.222	8.76
2	6.9	93	.320	.197	7.78
3	9	94	.293	.183	7.23
4	20	94	.185	.124	4.88
5	30.2	95	.122	.087	3.42
G-1	32.4	95	.112	.080	3.16
2	74.7	93	.027	.020	.77
3	87.4	94	.021	.014	.57
4	93.9	94	.019	.012	.49

Table B-6. *(continued)*

	Specific Ion Probe			Potentiometric Titration Predicted Values	
Sample Number	Reading (M-Volts)	Reaction Temperature (°F)	Calculated Chloride (%Cl-)	(%Cl-)	(lb/cu yd)
H-1	1.1	94	.411	.243	9.58
2	17.3	94	.207	.136	5.37
3	35	93	.100	.072	2.86
4	81.6	94	.024	.017	.65
5	82.9	93	.022	.016	.61
I-1	18.8	92	.193	.129	5.07
2	45.3	94	.068	.051	2.01
3	79.2	92	.024	.017	.66
4	80.2	92	.023	.016	.64
J-1	21.9	92	.169	.115	4.54
2	63.4	95	.038	.029	1.13
3	93.3	97	.021	.014	.56
4	93.1	97	.021	.014	.56
K-1	14.3	94	.234	.152	5.98
2	44.9	92	.068	.051	2.00
3	77.9	92	.024	.017	.68
4	83.8	92	.021	.015	.58
L-1	-4.7	96	.530	.300	11.82
2	-2.1	96	.474	.273	10.77
3	9.8	94	.283	.178	7.02
4	18.5	94	.197	.131	5.15
5	30.7	94	.119	.085	3.34
P1A-1	23.7	94	.144	.100	3.93
2	35.2	92	.089	.065	2.57
3	46.2	92	.058	.044	1.73
4	64.1	93	.033	.024	.96
P2-1	36	92	.086	.063	2.50
2	43.2	87	.062	.047	1.84
3	59.9	91	.036	.027	1.06
4	75.4	91	.023	.016	.64
P3-1	4.1	89	.329	.202	7.95
2	4.3	91	.327	.201	7.92
3	8.5	93	.273	.173	6.81
4	17.1	92	.188	.126	4.96

Table B-6. (*continued*)

	Specific Ion Probe			Potentiometric Titration Predicted Values	
Sample Number	Reading (M-Volts)	Reaction Temperature (°F)	Calculated Chloride (%Cl$^-$)	(%Cl$^-$)	(lb/cu yd)
C1-1	-.8	90	.409	.242	9.54
2	3.5	92	.339	.207	8.17
3	9.7	90	.258	.164	6.48
4	13.4	88	.218	.143	5.63
C2-1	LOST	LOST	LOST	LOST	LOST
2	2	92	.363	.219	8.63
3	4.1	91	.330	.202	7.98
4	7	92	.291	.182	7.19
B1-1	24.1	82	.134	.094	3.69
2	-2.4	89	.438	.256	10.10
3	29.6	89	.110	.079	3.10
4	-2.4	88	.438	.256	10.09
B2-1	37.7	92	.081	.060	2.35
2	69.1	94	.029	.021	.84
3	73.2	92	.025	.018	.71
4	86.4	94	.020	.014	.53
B3-1	59.4	90	.036	.027	1.06
2	82.5	91	.020	.013	.52
3	87.4	93	.019	.013	.50
4	87.2	92	.019	.012	.48

Table B-7. Predicted chloride content values for Virginia bridge VA I-81 over 670 NB.

	Specific Ion Probe			Potentiometric Titration Predicted Values	
Sample Number	Reading (M-Volts)	Reaction Temperature (°F)	Calculated Chloride (%Cl^-)	(%Cl^-)	(lb/cu yd)
A-1	-9.7	93	.615	.339	13.35
2	12.3	88	.232	.150	5.93
3	42.2	94	.070	.052	2.07
4	68.8	95	.030	.022	.88
5	97.5	96	.018	.012	.47
B-1	4.9	96	.326	.200	7.89
2	16.2	95	.200	.133	5.24
3	27.9	93	.122	.087	3.41
4	44.9	94	.064	.048	1.88
5	71.7	95	.028	.021	.81
C-1	5.6	93	.314	.194	7.65
2	28.6	93	.119	.084	3.33
3	62.2	94	.036	.027	1.06
4	100.5	97	.018	.012	.47
D-1	5.7	89	.310	.192	7.58
2	26	94	.133	.093	3.67
3	77.9	95	.025	.017	.69
4	98.5	95	.018	.011	.44
E-1	-4.7	90	.491	.282	11.10
2	15.5	94	.206	.136	5.36
3	63.6	96	.036	.027	1.05
4	83.5	94	.021	.015	.58
F-1	.5	93	.392	.234	9.21
2	20.9	96	.165	.113	4.44
3	76.6	96	.026	.019	.73
4	100.6	93	.016	.010	.38

Table B-7. (*continued*)

	Specific Ion Probe			Potentiometric Titration Predicted Values	
Sample Number	Reading (M-Volts)	Reaction Temperature (°F)	Calculated Chloride (%Cl$^-$)	(%Cl$^-$)	(lb/cu yd)
G-1	17	96	.194	.129	5.10
2	49.7	98	.056	.042	1.67
3	86.3	96	.022	.015	.58
4	88.8	94	.019	.013	.51
H-1	10.7	91	.255	.163	6.42
2	34.8	92	.095	.069	2.72
3	68.7	93	.030	.022	.88
4	101.8	92	.015	.009	.36
I-1	5.8	95	.317	.195	7.71
2	43.8	93	.068	.051	2.00
3	91.2	93	.019	.012	.48
4	96.2	94	.018	.012	.45
J-1	8.6	94	.280	.177	6.96
2	43.1	93	.070	.052	2.05
3	88.8	94	.020	.013	.53
4	89.9	94	.020	.013	.52
K-1	12.6	96	.238	.154	6.06
2	75.6	96	.027	.020	.78
3	91.6	96	.020	.014	.54
4	86.4	92	.020	.013	.52
L-1	8.8	93	.277	.175	6.90
2	39.7	91	.078	.058	2.27
3	60.6	90	.036	.027	1.08
4	85	94	.021	.015	.58
P1-1	3.3	84	.335	.205	8.08
2	10.6	88	.247	.158	6.25
3	13.2	91	.223	.145	5.73
4	18.1	90	.180	.121	4.79
P2-1	20.9	87	.159	.109	4.28
2	53	90	.046	.035	1.37
3	72.9	92	.026	.019	.74
4	81.8	89	.019	.013	.51

Table B-7. (*continued*)

	Specific Ion Probe			Potentiometric Titration Predicted Values	
Sample Number	Reading (M-Volts)	Reaction Temperature (°F)	Calculated Chloride (%Cl$^-$)	(%Cl$^-$)	(lb/cu yd)
P3-1	5.5	90	.308	.191	7.54
2	12.1	91	.233	.151	5.96
3	19.5	92	.171	.116	4.58
4	32.3	90	.101	.073	2.87
B1-1	13.2	88	.221	.144	5.69
2	87.9	92	.019	.012	.49
3	72	90	.025	.018	.72
4	80.3	90	.021	.014	.55
B2-1	31.4	89	.112	.080	3.16
2	82.7	90	.022	.015	.60
3	91.8	94	.021	.014	.55
4	96.3	96	.020	.014	.54
B3-1	3.5	88	.339	.207	8.17
2	31.8	86	.108	.078	3.07
3	55.3	90	.048	.036	1.42
4	69.2	91	.032	.023	.92
C1-1	-10.9	94	.617	.340	13.39
2	-4	86	.460	.267	10.52
3	5.3	90	.317	.195	7.71
4	14.4	90	.219	.143	5.66
C2-1	28.4	86	.124	.088	3.45
2	16.5	86	.199	.132	5.21
3	25.6	89	.140	.098	3.85
4	26	90	.139	.097	3.81

Table B-8. Predicted chloride content values for Florida bridge FL 206.

	Specific Ion Probe			Potentiometric Titration Predicted Values	
Sample Number	Reading (M-Volts)	Reaction Temperature (°F)	Calculated Chloride (%Cl-)	(%Cl-)	(lb/cu yd)
PC-1	-21.1	83	.828	.432	17.04
2	-19.1	85	.763	.404	15.94
3	-9.1	81	.502	.286	11.29
4	-4.4	81	.413	.244	9.61
5	-3.6	83	.401	.238	9.37
6	7	82	.258	.165	6.49
PC2-1	2	82	.317	.196	7.72
2	14.6	81	.188	.126	4.97
3	42.4	82	.062	.047	1.84
4	48.5	80	.048	.036	1.43
5	62.5	83	.030	.022	.88
6	85.9	82	.014	.008	.31
PO1-1	-7.2	81	.464	.268	10.58
2	-1.1	87	.364	.220	8.65
3	9.3	86	.237	.153	6.05
4	26.1	83	.119	.085	3.34
5	47.5	82	.051	.039	1.52
6	77.7	84	.019	.013	.50
PO2-1	46.7	83	.053	.040	1.59
2	64.7	85	.029	.021	.85
3	101.2	85	.012	.006	.22
4	111.7	82	.008	.002	.07
5	104	81	.008	.002	.09
P5-1	-22.7	84	.883	.455	17.95
2	-13.7	84	.610	.336	13.26
3	-6.9	86	.463	.268	10.57
4	2.4	85	.316	.195	7.70
5	20.8	82	.149	.103	4.06
P6-1	-1.6	80	.369	.222	8.76
2	-.7	80	.356	.215	8.49
3	LOST	LOST	LOST	LOST	LOST
4	36	80	.080	.059	2.34
5	59.9	85	.035	.026	1.04

Table B-8. (*continued*)

	Specific Ion Probe			Potentiometric Titration Predicted Values	
Sample Number	Reading (M-Volts)	Reaction Temperature (°F)	Calculated Chloride (%Cl-)	(%Cl-)	(lb/cu yd)
C1-1	39.4	83	.072	.054	2.12
2	58.2	84	.037	.028	1.09
3	66.7	82	.026	.019	.75
4	75.1	85	.022	.015	.60
5	83.2	83	.016	.010	.40
B1-1	68.1	82	.025	.018	.71
2	75.8	83	.020	.014	.54
3	90.8	85	.015	.009	.34
4	108.1	83	.009	.003	.13
5	113.8	83	.008	.002	.09
B2-1	55.7	81	.038	.029	1.13
2	71	81	.022	.015	.61
3	85.1	83	.015	.009	.37
4	101.7	82	.010	.004	.15
DA-1	74	90	.028	.020	.79
2	91.4	87	.017	.010	.41
3	97.5	91	.017	.011	.43
4	98	89	.016	.010	.38
DB-1	77.3	90	.025	.018	.72
2	92.1	92	.020	.013	.52
3	96.7	92	.018	.012	.46
4	98.5	89	.016	.010	.38
DC-1	79.3	91	.025	.018	.70
2	LOST		LOST	LOST	LOST
3	94.9	91	.018	.012	.46
4	97.6	92	.018	.012	.46
5	98.4	92	.018	.011	.45
DD-1	75.5	95	.030	.022	.86
2	82.9	94	.025	.018	.69
3	92.8	91	.019	.012	.49
4	99.2	93	.010	.012	.46

Table B-9. Predicted chloride content values for Florida bridge FL 295 EB.

	Specific Ion Probe			Potentiometric Titration Predicted Values	
Sample Number	Reading (M-Volts)	Reaction Temperature (°F)	Calculated Chloride (%Cl^-)	(%Cl^-)	(lb/cu yd)
P1-1	15.3	81	.188	.126	4.95
2	28.6	78	.107	.077	3.02
3	41.2	80	.065	.048	1.91
4	53.8	82	.041	.031	1.21
5	56.6	81	.036	.027	1.06
P2-1	68.5	83	.025	.018	.69
2	81.3	83	.017	.010	.41
3	89.2	81	.012	.006	.24
4	95.7	80	.010	.003	.14
P3-1	11	83	.226	.147	5.79
2	25.2	81	.125	.088	3.47
3	39.8	84	.071	.053	2.09
4	53.8	81	.040	.030	1.19
5	57.5	82	.035	.027	1.05
P4-1	66.6	82	.026	.018	.73
2	79.7	85	.019	.012	.49
3	96.6	84	.012	.006	.23
4	101.7	82	.009	.003	.13
B1-1	91.6	83	.013	.007	.26
2	104	84	.010	.004	.17
3	113.9	84	.009	.003	.11
4	118.5	85	.009	.003	.12
B2-1	81.3	81	.015	.009	.36
2	100.7	82	.010	.004	.14
3	116.1	83	.008	.002	.07
4	120.3	80	.006	0	0

Table B-9. (*continued*)

	Specific Ion Probe			Potentiometric Titration Predicted Values	
Sample Number	Reading (M-Volts)	Reaction Temperature (°F)	Calculated Chloride (%Cl^-)	(%Cl^-)	(lb/cu yd)
C1-1	85	82	.014	.008	.32
2	106.8	83	.009	.003	.12
3	109.7	83	.009	.003	.10
4	114	83	.008	.002	.08
C2-1	93.9	85	.013	.007	.28
2	103.4	83	.010	.004	.15
3	108.4	84	.010	.004	.14
4	114.9	84	.009	.003	.10
C3-1	76.5	84	.020	.013	.52
2	90.6	82	.012	.006	.25
3	104.9	83	.010	.003	.14
4	106.6	85	.011	.004	.18
C4-1	81	85	.018	.012	.46
2	102.9	86	.012	.006	.23
3	114.5	82	.008	.001	.05
4	114.4	80	.006	0	0
C5-1	78.6	86	.020	.013	.53
2	101.8	81	.009	.003	.11
3	117.5	78	.005	0	0
4	121.5	78	.004	0	0
C6-1	83.5	84	.016	.010	.40
2	104.4	83	.010	.004	.14
3	113.4	84	.009	.003	.11
4	121.2	78	.004	0	0

Table B-10. Predicted chloride content values for Florida bridge FL 312.

	Specific Ion Probe			Potentiometric Titration Predicted Values	
Sample Number	Reading (M-Volts)	Reaction Temperature (°F)	Calculated Chloride (%Cl^-)	(%Cl^-)	(lb/cu yd)
P1-1	-10.1	85	.509	.290	11.43
2	-.3	83	.341	.208	8.20
3	9.7	84	.228	.148	5.85
4	17.5	84	.167	.114	4.48
5	29.7	83	.103	.074	2.92
6	62.8	84	.031	.023	.90
P2-1	7.9	84	.245	.158	6.22
2	18	85	.164	.112	4.42
3	24.1	86	.130	.091	3.60
4	35.9	83	.081	.060	2.35
5	52.3	84	.044	.034	1.32
6	76.8	84	.020	.014	.53
P3-1	21.9	85	.141	.098	3.87
2	36	85	.082	.060	2.38
3	57.2	83	.037	.028	1.09
4	84.1	82	.015	.009	.35
5	95.3	84	.013	.007	.26
6	96.5	84	.012	.006	.25
F1-1	-22	83	.826	.431	17.00
2	-18.9	85	.729	.389	15.35
3	-16.7	85	.666	.362	14.26
4	-.7	86	.348	.212	8.35
5	2.4	87	.308	.191	7.53
6	16.9	86	.172	.117	4.60
F2-1	-29.9	86	1.144	.562	22.16
2	-22.6	87	.849	.441	17.39
3	-9.8	83	.502	.286	11.29
4	-9	83	.486	.279	10.99
5	-4	87	.399	.237	9.34
6	11.7	86	.212	.139	5.49
B1-1	99.1	88	.015	.009	.35
2	115.3	90	.013	.007	.28
3	118.6	86	.010	.004	.16
4	110.7	88	.013	.007	.26

Table B-10. (*continued*)

	Specific Ion Probe			Potentiometric Titration Predicted Values	
Sample Number	Reading (M-Volts)	Reaction Temperature (°F)	Calculated Chloride (%Cl^-)	(%Cl^-)	(lb/cu yd)
B1A-1	95.5	91	.018	.012	.46
2	108.6	91	.015	.009	.34
3	119.4	93	.015	.008	.33
4	121.6	92	.014	.008	.30
C1-1	54.5	87	.048	.036	1.43
2	60	91	.042	.032	1.26
3	62.8	90	.038	.029	1.13
4	74.1	90	.028	.020	.80
5	86.9	93	.022	.016	.61
6	96.9	94	.019	.013	.51
C2-1	74.4	91	.028	.021	.81
2	77.2	93	.027	.020	.79
3	84.2	93	.024	.017	.65
4	90	91	.020	.013	.52
DA-1	72.6	93	.031	.023	.89
2	80.9	91	.024	.017	.67
3	95.5	90	.017	.011	.43
4	94.8	93	.019	.013	.51
DB-1	73.5	91	.029	.021	.83
2	86	89	.020	.014	.54
3	93.5	89	.017	.011	.43
4	94.1	89	.017	.011	.43

Table B-11. Predicted chloride content values for Wisconsin bridge WI 243 WB.

	Specific Ion Probe			Potentiometric Titration Predicted Values	
Sample Number	Reading (M-Volts)	Reaction Temperature (°F)	Calculated Chloride (%Cl^-)	(%Cl^-)	(lb/cu yd)
A-1	-6.3	87	.521	.296	11.65
2	11.8	87	.244	.157	6.19
3	23	88	.155	.106	4.19
4	42.5	88	.072	.053	2.11
5	72.4	89	.027	.019	.76
B-1	-8.8	90	.581	.323	12.74
2	-1.8	91	.434	.254	10.01
3	18	92	.192	.128	5.05
4	46.6	90	.063	.047	1.86
5	38.9	88	.082	.061	2.39
C-1	-16.1	92	.792	.417	16.43
2	-3.9	89	.472	.273	10.74
3	22.9	91	.157	.108	4.25
4	43.9	94	.072	.053	2.11
5	70.3	95	.032	.024	.94
D-1	-12.9	89	.690	.372	14.68
2	1.1	92	.385	.230	9.07
3	26	91	.139	.097	3.82
4	51.1	90	.054	.040	1.59
5	32.4	83	.103	.074	2.93
E-1	-11	91	.638	.349	13.76
2	5	91	.327	.201	7.91
3	19.9	89	.176	.119	4.69
4	54.1	89	.048	.036	1.42
5	55.7	90	.046	.034	1.36
F-1	-3.1	92	.458	.266	10.48
2	5.1	92	.326	.200	7.89
3	18.9	90	.184	.124	4.87
4	40.9	94	.080	.059	2.33
5	42.3	85	.070	.053	2.07
G-1	-6.1	90	.519	.294	11.61
2	5.6	94	.320	.197	7.78
3	17.7	94	.196	.130	5.13
4	38.2	94	.088	.065	2.55
5	48.8	93	.060	.045	1.78

Table B-11. (*continued*)

	Specific Ion Probe			Potentiometric Titration Predicted Values	
Sample Number	Reading (M-Volts)	Reaction Temperature (°F)	Calculated Chloride (%Cl$^-$)	(%Cl$^-$)	(lb/cu yd)
H-1	-8.3	93	.571	.319	12.56
2	4.1	92	.340	.207	8.17
3	18.2	95	.192	.128	5.06
4	37.8	90	.087	.064	2.52
5	45.6	87	.063	.047	1.87
I-1	-16.3	94	.800	.420	16.56
2	-6.5	94	.530	.300	11.81
3	11.4	90	.250	.160	6.32
4	37.4	91	.089	.065	2.57
5	61.6	92	.039	.029	1.15
J-1	-11.3	93	.647	.353	13.93
2	-2	90	.437	.255	10.07
3	11.8	92	.242	.156	6.15
4	40.9	95	.082	.061	2.39
5	50.3	91	.058	.043	1.71
K-1	-14.5	91	.694	.374	14.74
2	5.1	87	.312	.193	7.62
3	11.3	92	.247	.159	6.25
4	32.7	93	.109	.078	3.09
5	58.9	90	.043	.032	1.27
L-1	-9.9	90	.575	.321	12.64
2	-1.8	90	.415	.245	9.65
3	9.4	90	.265	.168	6.63
4	20.4	93	.174	.117	4.63
5	47.8	88	.061	.046	1.80

Table B-11. *(continued)*

	Specific Ion Probe			Potentiometric Titration Predicted Values	
Sample Number	Reading (M-Volts)	Reaction Temperature (°F)	Calculated Chloride (%Cl-)	(%Cl-)	(lb/cu yd)
A1-1	52.7	99	.058	.043	1.71
2	63	99	.043	.032	1.26
3	72.3	104	.037	.027	1.08
4	68.7	102	.038	.029	1.14
A2-1	39.1	102	.092	.067	2.65
2	56.2	104	.055	.041	1.62
3	73.2	105	.036	.027	1.08
4	75.7	102	.033	.024	.96
PC1-1	41.2	97	.083	.061	2.41
2	58.1	103	.051	.039	1.52
3	75.5	104	.034	.026	1.01
4	55.7	102	.054	.041	1.61
PC2-1	47.6	96	.066	.049	1.94
2	57.2	100	.051	.038	1.51
3	59	98	.047	.035	1.40
4	60.9	101	.046	.035	1.38
PO1-1	40.3	93	.079	.059	2.31
2	56.8	101	.049	.037	1.46
3	59.2	102	.046	.035	1.38
4	64.3	103	.041	.031	1.22
PO2-1	51.4	97	.056	.042	1.67
2	76.3	97	.028	.021	.81
3	70.9	96	.031	.023	.92
4	39.6	91	.081	.060	2.35

Table B-12. Predicted chloride content values for Wisconsin bridge WI 245 WB.

	Specific Ion Probe			Potentiometric Titration Predicted Values	
Sample Number	Reading (M-Volts)	Reaction Temperature (^{O}F)	Calculated Chloride ($\%Cl^{-}$)	($\%Cl^{-}$)	(lb/cu yd)
A-1	-14.4	91	.673	.365	14.37
2	.2	87	.371	.223	8.79
3	1.4	90	.355	.215	8.48
4	15	90	.207	.137	5.38
5	31.5	92	.111	.079	3.13
B-1	14.4	83	.207	.137	5.39
2	16.8	88	.192	.128	5.04
3	12.9	92	.226	.147	5.80
4	20	90	.170	.116	4.55
5	49.3	92	.059	.044	1.75
C-1	-7.2	95	.505	.288	11.36
2	.3	97	.376	.225	8.88
3	12.7	94	.229	.149	5.87
4	27.8	95	.129	.091	3.58
5	58.9	95	.045	.034	1.35
D-1	-13.6	96	.718	.385	15.16
2	10.3	88	.259	.165	6.51
3	13.2	94	.233	.151	5.96
4	37	95	.092	.067	2.64
5	65.8	96	.036	.027	1.07
E-1	-7.3	100	.552	.310	12.23
2	3.1	94	.354	.215	8.46
3	21.5	97	.168	.114	4.51
4	49	96	.060	.045	1.79
5	67.9	95	.034	.025	.99
F-1	-7.3	98	.551	.310	12.20
2	7.1	90	.297	.186	7.31
3	18.9	96	.186	.125	4.92
4	28.4	88	.123	.087	3.43
5	61.6	94	.040	.030	1.17
G-1	-14.9	91	.756	.401	15.81
2	-1.1	91	.421	.248	9.76
3	6.6	96	.292	.183	7.21
4	26.2	94	.138	.096	3.80
5	49.7	95	.058	.044	1.73

Table B-12. (*continued*)

	Specific Ion Probe			Potentiometric Titration Predicted Values	
Sample Number	Reading (M-Volts)	Reaction Temperature ($^{\circ}$F)	Calculated Chloride (%Cl^-)	(%Cl^-)	(lb/cu yd)
H-1	-14	90	.661	.360	14.17
2	-4.9	92	.459	.266	10.49
3	9.2	89	.260	.165	6.52
4	47.2	90	.062	.047	1.84
5	66.8	93	.035	.026	1.03
I-1	-4.6	89	.451	.263	10.35
2	-1	93	.393	.234	9.23
3	12.3	93	.232	.151	5.93
4	31.5	88	.108	.078	3.07
5	51	91	.055	.042	1.64
J-1	-9	90	.540	.304	12.00
2	.9	92	.364	.219	8.65
3	16.4	96	.200	.132	5.22
4	36.6	97	.095	.069	2.73
5	57.8	94	.046	.035	1.37
K-1	-14.7	95	.683	.369	14.56
2	-4.5	95	.453	.263	10.39
3	8.8	94	.267	.169	6.68
4	23.5	94	.151	.104	4.11
5	36	86	.090	.066	2.60
L-1	-9.5	94	.553	.311	12.25
2	5.7	93	.301	.187	7.39
3	19.7	91	.173	.117	4.61
4	45.8	91	.066	.049	1.94
5	72.4	93	.030	.022	.88

Table B-12. (*continued*)

	Specific Ion Probe			Potentiometric Titration Predicted Values	
Sample Number	Reading (M-Volts)	Reaction Temperature (^{O}F)	Calculated Chloride (%Cl$^-$)	(%Cl$^-$)	(lb/cu yd)
PO-1	3.5	87	.369	.222	8.76
2	5.7	91	.341	.208	8.19
3	18.4	89	.205	.136	5.35
4	34.6	88	.110	.079	3.10
5	62.6	86	.039	.030	1.17
PO2-1	39.9	88	.090	.066	2.59
2	58.3	88	.047	.035	1.40
3	60.5	88	.044	.033	1.30
4	47.6	87	.067	.050	1.98
5	68.7	87	.033	.025	.97
PC1-1	-11.2	89	.669	.363	14.31
2	1.5	87	.400	.238	9.37
3	8.3	88	.305	.190	7.48
4	28.4	84	.136	.095	3.75
5	36.9	91	.102	.074	2.91
6	65.7	92	.039	.030	1.17
PC2-1	25.4	95	.160	.110	4.32
2	35.8	88	.171	.116	4.57
3	53.7	93	.058	.044	1.72
4	60.9	88	.043	.032	1.28
5	62.7	91	.042	.032	1.26
A1-1	49.4	97	.069	.052	2.04
2	64.3	100	.046	.035	1.37
3	61.9	98	.048	.036	1.42
4	47.8	91	.069	.052	2.04
5	67.5	102	.040	.030	1.19
A2-1	23.1	95	.162	.111	4.36
2	34.4	102	.110	.079	3.10
3	59.2	103	.050	.038	1.50
4	64.2	101	.043	.032	1.28
5	78	97	.029	.021	.84

Table B-13. Predicted chloride content values for Wisconsin bridge WI 252.

	Specific Ion Probe			Potentiometric Titration Predicted Values	
Sample Number	Reading (M-Volts)	Reaction Temperature (^{o}F)	Calculated Chloride (%Cl$^-$)	(%Cl$^-$)	(lb/cu yd)
A-1	-18.8	88	.785	.414	16.32
2	-7	84	.479	.276	10.86
3	-4.9	91	.443	.258	10.19
4	7.5	86	.264	.168	6.61
5	28.1	80	.111	.079	3.13
6	42.1	84	.066	.049	1.94
B-1	-26.9	89	1.102	.546	21.50
2	-16.6	89	.717	.384	15.15
3	-5.6	90	.455	.264	10.42
4	5	88	.294	.183	7.23
5	19	88	.167	.113	4.47
6	46.4	87	.058	.043	1.71
C-1	-12	86	.591	.328	12.92
2	-10.4	92	.556	.312	12.30
3	1.5	92	.341	.208	8.21
4	7.5	86	.264	.168	6.61
5	32.2	84	.097	.070	2.77
6	49.2	86	.052	.039	1.54
D-1	-20.4	89	.840	.437	17.24
2	-17.9	89	.757	.402	15.83
3	-12.4	93	.605	.334	13.17
4	-1.2	91	.381	.228	8.98
5	11.7	88	.223	.146	5.75
6	43.5	92	.067	.050	1.98
E-1	-21.2	89	.869	.449	17.72
2	-9.5	91	.535	.302	11.92
3	-4.6	92	.438	.256	10.10
4	6.2	92	.282	.177	6.99
5	27.4	91	.121	.086	3.39
6	57.6	90	.041	.031	1.22
F-1	-19.3	94	.806	.423	16.66
2	-11	90	.569	.318	12.53
3	-1.1	91	.379	.227	8.95
4	13.5	99	.215	.141	5.55
5	26.8	91	.124	.088	3.46
6	44.7	87	.061	.046	1.82

Table B-13. (*continued*)

	Specific Ion Probe			Potentiometric Titration Predicted Values	
Sample Number	Reading (M-Volts)	Reaction Temperature (^{O}F)	Calculated Chloride (%Cl$^-$)	(%Cl$^-$)	(lb/cu yd)
G-1	-25.6	93	1.046	.523	20.61
2	-22.3	92	.911	.467	18.42
3	-15.5	87	.684	.370	14.57
4	4.1	91	.306	.190	7.50
5	14.4	91	.202	.134	5.28
6	44.7	86	.061	.046	1.80
H-1	-18.1	87	.762	.404	15.92
2	-9.7	87	.537	.303	11.95
3	-3.8	92	.424	.249	9.83
4	-.3	90	.366	.221	8.70
5	18	90	.175	.118	4.65
6	50.9	92	.052	.039	1.56
I-1	-19.7	91	.817	.428	16.86
2	-15.6	92	.690	.372	14.67
3	.6	90	.353	.214	8.44
4	5.2	93	.294	.184	7.25
5	24.7	93	.136	.095	3.75
6	55.1	92	.046	.034	1.36
J-1	-16.9	87	.725	.388	15.28
2	-15.2	88	.676	.366	14.43
3	-7	88	.481	.277	10.91
4	2.2	88	.329	.202	7.96
5	13.6	88	.207	.137	5.38
6	40.8	89	.072	.054	2.12
K-1	-17.3	91	.740	.394	15.54
2	-10.6	88	.558	.313	12.34
3	-1.5	90	.385	.230	9.06
4	16.6	89	.184	.123	4.87
5	28.7	94	.117	.083	3.29
6	53.8	88	.045	.034	1.34
L-1	-18.6	88	.779	.411	16.21
2	-11.7	89	.585	.325	12.82
3	-9.8	88	.540	.305	12.00
4	1.1	89	.345	.210	8.28
5	12.2	88	.219	.143	5.65
6	36.6	91	.086	.063	2.48

Table B-13. (*continued*)

	Specific Ion Probe			Potentiometric Titration Predicted Values	
Sample Number	Reading (M-Volts)	Reaction Temperature (°F)	Calculated Chloride $(\%\text{Cl}^-)$	$(\%\text{Cl}^-)$	(lb/cu yd)
P1-1	-.6	98	.420	.247	9.74
2	3.3	103	.361	.218	8.60
3	18	99	.200	.133	5.23
4	34.6	101	.108	.078	3.07
5	44.5	104	.079	.058	2.30
P2-1	26.8	104	.146	.101	3.98
2	39.4	102	.092	.067	2.65
3	49.4	104	.068	.050	1.99
4	58.1	99	.050	.037	1.47
5	59.1	103	.050	.038	1.50
BW1-1	-23.8	93	1.051	.525	20.69
2	-7.2	91	.533	.301	11.87
3	7.1	88	.297	.185	7.31
4	-1.1	92	.417	.246	9.69
5	.6	93	.390	.232	9.16
BW2-1	-21.4	94	.953	.485	19.11
2	-14	93	.704	.378	14.92
3	-5.3	93	.494	.283	11.16
4	-1.5	90	.422	.248	9.79
5	2.2	93	.365	.220	8.69
A1B-1	-7.8	95	.548	.308	12.15
2	12.6	97	.244	.157	6.19
3	26.1	100	.147	.102	4.02
4	38.4	95	.092	.067	2.64
5	55.4	94	.051	.039	1.53
A1Cl-1	-19.9	93	.896	.461	18.16
2	-10.7	95	.617	.340	13.38
3	-2.4	94	.440	.257	10.14
4	11.9	94	.249	.160	6.30
5	30	94	.124	.088	3.46

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