

FINAL REPORT

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**AN ALTERNATIVE  
POTENTIOMETRIC METHOD  
FOR DETERMINING CHLORIDE CONTENT  
IN CONCRETE SAMPLES  
FROM REINFORCED CONCRETE BRIDGES**

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<p>16. Abstract</p> <p>Analysis of chloride contents in ground concrete samples collected from reinforced-concrete bridges and other structures exposed to deicing salts or seawater has become an important part of the inspection for such structures. Such an analysis provides important information for deciding what measures to implement to protect and rehabilitate such structures. As an alternative to the standard potentiometric-titration method of chloride analysis for concrete samples, which is time-consuming and expensive, this study developed and evaluated a new, simple, short method called internal calibration. With this method, cold digested solutions of concrete samples are spiked twice with a relatively small and precisely measured amount of a standard NaCl solution and the chloride content of each sample is calculated from the potential readings before and after the spiking by an equation derived from the Nernst equation.</p> <p>A comparison of the results from analyses of concrete samples using the standard method and the new method showed that the chloride concentration determinations are lower with the new method. However, at chloride contents around the chloride corrosion threshold, i.e., 0.00 to 2.00 kg/m<sup>3</sup>, which is the range of most interest in decisions regarding rehabilitation, the differences between the methods were almost negligible.</p> <p>When the time and reagents required are considered, the cost of using the new method is relatively low, less than 25 percent of the cost of using the standard method. This does not include the indirect savings resulting from eliminating the need to use and properly dispose of potentially hazardous reagents and waste. Since the new method does not require the extensive glassware required with the standard method, and the digestion solution and standard NaCl solution can be prepackaged, concrete samples can be analyzed by trained field units.</p>			
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## ABSTRACT

Analysis of chloride contents in ground concrete samples collected from reinforced-concrete bridges and other structures exposed to deicing salts or seawater has become an important part of the inspection for such structures. Such an analysis provides important information for deciding what measures to implement to protect and rehabilitate such structures. As an alternative to the standard potentiometric-titration method of chloride analysis for concrete samples, which is time-consuming and expensive, this study developed and evaluated a new, simple, short method called internal calibration. With this method, cold digested solutions of concrete samples are spiked twice with a relatively small and precisely measured amount of a standard NaCl solution and the chloride content of each sample is calculated from the potential readings before and after the spiking by an equation derived from the Nernst equation.

A comparison of the results from analyses of concrete samples using the standard method and the new method showed that the chloride concentration determinations are lower with the new method. However, at chloride contents around the chloride corrosion threshold, i.e., 0.00 to 2.00 kg/m<sup>3</sup>, which is the range of most interest in decisions regarding rehabilitation, the differences between the methods were almost negligible.

When the time and reagents required are considered, the cost of using the new method is relatively low, less than 25 percent of the cost of using the standard method. This does not include the indirect savings resulting from eliminating the need to use and properly dispose of potentially hazardous reagents and waste. Since the new method does not require the extensive glassware required with the standard method, and the digestion solution and standard NaCl solution can be prepackaged, concrete samples can be analyzed by trained field units.



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## INTRODUCTION

Reinforced-concrete bridges exposed to deicing salts and seawater are susceptible to intrusion by the corrosive chloride ions in these substances. In the early 1970s, it became clear that when the concentration of chloride ions in the concrete immediately surrounding the reinforcing steel exceeds a threshold level, corrosion of the reinforcing steel sets in, and if not remedied, leads to premature deterioration of the structures. Since the threshold is influenced by many factors in the concrete, such as the type of cement used, pH of the concrete, presence of oxygen and moisture, etc., several threshold values have been reported by different investigators.<sup>1-4</sup> However, the most widely applied corrosion threshold is 0.033 percent Cl<sup>-</sup> by weight (0.78 kg/m<sup>3</sup>) of concrete, which resulted from work conducted in Federal Highway Administration (FHWA) laboratories.<sup>4</sup>

Because of the critical role of chloride ions in the corrosion of reinforcing steel, the determination of the concentration of chloride ions that have accumulated in reinforced-concrete bridges exposed to deicing salts and seawater has become an integral part of the inspection methods used in routine bridge condition surveys. The standard test methods used for this analysis are AASHTO T-260, Sampling and Testing for Chloride Ion in Concrete and Concrete Raw Materials, which is based on work in the 19790s at FHWA and elsewhere,<sup>5,6</sup> and the equivalent ASTM C-1152, Acid-Soluble Chloride in Mortar and Concrete. These methods use the technique of potentiometric titration, which involves (1) extraction of the chloride ions by digestion of a weighed portion of a ground concrete sample in a boiling nitric acid solution and separation of the resulting acid digest from the solid residue by filtration, followed by (2) titration of the extracted chloride ions in the filtrate with a standardized silver nitrate solution. As the standard silver nitrate solution is being added incrementally, the chloride ions are precipitated as silver chloride



and the potential of the filtrate is monitored by either a chloride or a silver ion-specific electrode. This allows the endpoint, which is the amount of silver nitrate required to precipitate all chloride ions extracted from the concrete sample, to be determined. From this endpoint, the concentration

of chloride in the concrete sample can be calculated. Although the method is quite adequate, the entire procedure is lengthy and laborious; some laboratories charge \$50 to \$75, or more, per concrete sample. Since the inspection of each bridge usually requires numerous samples taken from different locations, the cost of surveying a bridge can be high if the bridge is large. Consequently, there have been commercial attempts in the late 1980s to provide a quicker alternative method.

Most notable of these attempts are two chloride analysis kits, which have been purported to provide rapid and accurate analysis of powdered concrete samples without the need to send the samples to a laboratory. Theoretically, the prescribed procedures are simple. These procedures essentially involve cold digestion of a weighed amount of a ground concrete sample in a proprietary digestion solution, followed by measurement of the potential ( $E_x$ ) of the resulting solution with a supplied ion-specific electrode. The concentration of the chloride ion in the concrete sample ( $C_x$ ) is then calculated from  $E_x$  using a calibration curve:

$$E_x = K + S \cdot \text{Log}C_x \quad [2]$$

which is basically the Nernst equation (Figure 1). The two associated parameters  $K$  and  $S$ , which are the reference potential and the response slope of the electrode, respectively, are determined by making similar potential measurements on three or four standard solutions of different known chloride concentrations that are typically supplied in each kit. In essence, these rapid methods use only the first reading of a potentiometric titration—that is, the first potential reading before addition of any titrant—to determine the chloride content of a sample. These rapid test kits, however, have been found in separate independent investigations to give inconsistent results.<sup>7,8</sup>

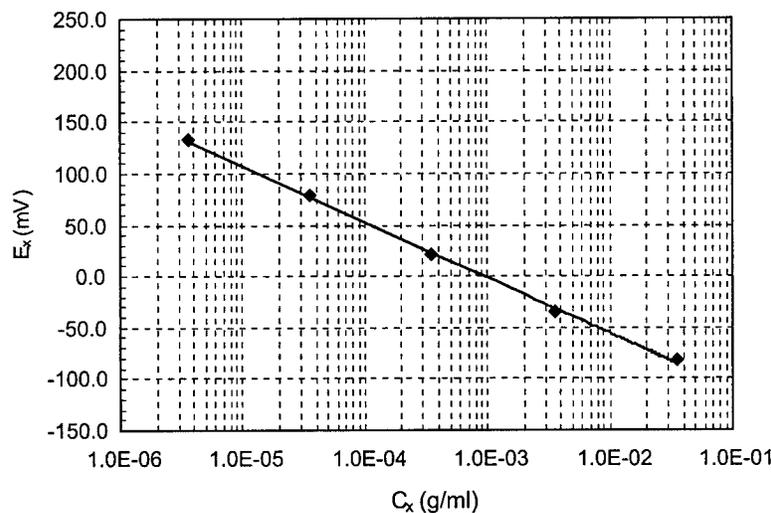


Figure 1. Calibration Curve Relating Concentration of Chloride Ions to Electrode Potential

### PURPOSE AND SCOPE

The purpose of this study was to develop an alternative simpler and shorter method to determine the concentration of chloride ions in ground concrete samples.

## METHODS

### Derivation

The authors postulated that the previously described reported inconsistency of the test kits<sup>7,8</sup> lies in the inapplicability of the calibration curve or the values of the two parameters  $K$  and  $S$  in Eq. 1 to all possible concrete samples. The potential of a digested concrete sample solution, as measured by a chloride-specific electrode, should ideally be influenced only by the amount of chloride ions present. However, this potential can also be influenced, to some extent, by the species and amounts of some other ions than can come from the cement and aggregates used to make a concrete. Therefore, any series of standard solutions to be used for calibration purposes should be as identical in ionic composition in all aspects as all possible concrete samples that can be encountered. Otherwise,  $K$  and  $S$  would not be universally applicable to all possible concrete samples. Considering that the sources of cement and aggregates that can be used for making concrete are so varied, it is impossible to prepare a series of standard chloride solutions that contain all the other ions that may be encountered in any digested concrete sample.

This shortcoming can be eliminated by not using a prepackaged series of standard solutions to obtain a calibration curve. Instead, a calibration can be performed with the digested solution of each pulverized concrete sample through adding a precise amount of a standard chloride solution. Therefore, the authors called this alternative procedure “internal calibration.” Mathematically, if given a measured volume  $V_x$  (mL) of a digested concrete solution containing an unknown amount  $W_x$  (g) of chloride ions, the concentration of the chloride ions would be

$$C_x = \left( \frac{W_x}{V_x} \right) \quad [3]$$

According to Eq. 2, the potential of this solution,  $E_x$ , as measured by an ion-specific electrode, would be related to  $C_x$  as follows:

$$E_x = K + S \cdot \text{Log} C_x = K + S \cdot \text{Log} \left( \frac{W_x}{V_x} \right) \quad [4]$$

If to this unknown solution is added a relatively small volume,  $V_s$ , of a standard chloride solution with a chloride concentration of  $C_s$ ,

$$C_s = \left( \frac{W_s}{V_s} \right) \quad [5]$$

the new potential of the resulting solution would be

$$E_{x+s} = K + S \cdot \text{Log} [C_{x+s}] = K + S \cdot \text{Log} \left[ \frac{W_{x+s}}{V_{x+s}} \right] \quad [6]$$

and

$$W_{x+S} = W_x + W_s \quad [7]$$

where  $V_{x+S}$  and  $W_{x+S}$  are the new volume and the total amount of chloride ions, respectively, in the new solution.

If the volume of the standard solution added is only a small fraction of the original volume of the concrete solution so that  $V_x \gg V_s$ , then  $V_{x+S} = V_x + V_s \cong V_x$  and Eq. 6 becomes

$$E_{x+S} = K + S \cdot \text{Log} \left( \frac{W_x + W_s}{V_x} \right) = K + S \cdot \text{Log} C_x' \quad [8]$$

Similarly, if a second aliquot portion ( $V_s$ ) of this standard solution is added to the concrete solution, then

$$E_{x+2S} = K + S \cdot \text{Log} \left( \frac{W_x + 2W_s}{V_x} \right) = K + S \cdot \text{Log} C_x'' \quad [9]$$

By solving for  $K$  in Eqs. 2 and 8 and equating the resulting equations

$$E_x - S \cdot \text{Log} C_x = E_{x+S} - S \cdot \text{Log} C_x' \quad [10]$$

Solving for  $S$  yields

$$S = \frac{[E_x - E_{x+S}]}{\text{Log} \left[ \frac{C_x}{C_x'} \right]} \quad [11]$$

Similarly, from Eqs. 2 and 9

$$S = \frac{[E_x - E_{x+2S}]}{\text{Log} \left[ \frac{C_x}{C_x''} \right]} \quad [12]$$

Equating the last two relationships yields

$$\frac{[E_x - E_{x+S}]}{[E_x - E_{x+2S}]} = \frac{\text{Log} C_x - \text{Log} C_x'}{\text{Log} C_x - \text{Log} C_x''} \quad [13]$$

In an analysis, only  $C_x$  is the unknown in Eq. 13 since all other variables are measured. Even though there is no direct solution for  $C_x$ , the latter can be determined numerically.

The left and right ratios in Eq. 12 may be defined as follows:

$$R_l = R_r$$

or

$$R_l - R_r = 0 \quad [14]$$

To arrive at the sought-for value of  $C_x$ , one must first define:

$$C_A = 0.01 \text{ (or any larger initial value except 0.00)} \quad [15]$$

where  $C_A$  is the first assumed value for  $C_x$ . Then, one must substitute  $C_x$  in Eq. 13 by  $C_A$  and calculate the value of  $R_r$ . If this  $R_r$  satisfies the condition in Eq. 13, then 0.01 unit of concentration is the sought-for chloride concentration of the concrete sample being analyzed. Otherwise, the amount of  $C_A$  may be increased by an increment, i.e.,

$$C_A \rightarrow C_A + I \quad [16]$$

Then, one may iteratively calculate  $R_r$  and increase the value of  $C_A$  until the condition in Eq. 13 is satisfied and the final assumed chloride concentration is the sought-for chloride concentration ( $C_x$ ) of the sample, i.e.,

$$\lim_{C_A \rightarrow C_x} (R_l - R_r) = 0 \quad [17]$$

The value of  $I$  can be the precision of the test, if already determined, or a practical unit of chloride concentration appropriate for the application (such as the 0.01 kg/m<sup>3</sup> in Eq. 15). These iterative calculations can be conducted without difficulty through use of a spreadsheet, as is demonstrated later.

### Test of the Concept

To validate this concept of internal calibration, five NaCl solutions, each with a different chloride concentration, were prepared for use as test solutions. The concentrations chosen represent a wide range (2 orders) of concentrations: 0.0001, 0.0005, 0.001, 0.005, and 0.01 M. A 25.00-mL portion of each solution would be equivalent to 0.003, 0.015, 0.030, 0.150, and 0.300 percent Cl<sup>-</sup> (0.07, 0.35, 0.70, 3.49, and 6.97 kg Cl<sup>-</sup>/m<sup>3</sup>), respectively, in a 3-g concrete sample, which is the nominal sample weight suggested in the standard method. These represent the range of chloride concentrations that are commonly encountered in concrete bridge decks. A 1.00 M Cl<sup>-</sup> solution was chosen as the standard solution.

At the beginning of the test of each solution, a 25.00-mL portion of the solution was transferred into a 150-mL beaker, followed by addition of 25 mL of de-ionized water. While the solution was being stirred with the aid of a stirring rod and magnetic stirrer, the potential ( $E_x$ ) of

the solution was measured with a chloride combination electrode. Then, a precisely measured 0.50-mL portion of the standard 1.00 M Cl<sup>-</sup> solution, which contained Cl<sup>-</sup> in an amount equivalent to 13.96 kg Cl<sup>-</sup>/m<sup>3</sup> for a 3.0-g concrete sample, was added and the potential ( $E_{x+S}$ ) of the solution was measured. A second 0.5-mL portion of the standard solution was added, and the new potential ( $E_{x+2S}$ ) measured. These procedures were repeated two more times for each test solution (see Table 1). Table 2 shows an example of the spreadsheet calculation involved to determine the true concentration of Cl<sup>-</sup> ( $C_x$ ) in Test 1. As explained previously, the sought-for  $C_x$  is the value that satisfies Eq. 14. The calculation started with  $C_A$  or assumed  $C_x$  set at 0.01 kg/m<sup>3</sup> (see Table 2). As this parameter was increased, the difference ( $R_l - R_p$ ) became smaller until it became 0 when the assumed  $C_A$  of 6.615 kg/m<sup>3</sup> was the “true” chloride concentration of the concrete solution.

After this concentration was rounded to 6.61 kg/m<sup>3</sup> and compared with the known Cl<sup>-</sup> concentration of 6.97 kg/m<sup>3</sup> of the test solution used, it was clear that this test was off by 0.36 kg/m<sup>3</sup> (see Test 1 in Table 1). Two additional tests of the same chloride solution yielded concentrations of 6.60 and 6.52 kg/m<sup>3</sup>; for the triplicate tests, the mean was 6.58 kg/m<sup>3</sup> and the standard deviation was 0.05 kg/m<sup>3</sup>. The mean error of results for this test solution with the

**Table 1. Validation of Concept of Internal Calibration, Using Chloride Solutions of Known Concentrations**

Test	Known				$E_x$ (mV)	$E_{x+S}$ (mV)	$E_{x+2S}$ (mV)	$R_l$	Calculated	
	$C_x$ (kg/m <sup>3</sup> )	$V_x$ (mL)	$C_S$ (kg/m <sup>3</sup> )	$V_S$ (mL)					$C_x$ (kg/m <sup>3</sup> )	Error (kg/m <sup>3</sup> )
1	6.97	25.00	13.96	0.50	134.7	106.0	92.9	0.68660	6.61	-0.36
2		25.00	13.96	0.50	134.4	105.9	92.9	0.68675	6.60	-0.37
3		25.00	13.96	0.50	134.2	105.8	92.9	0.68765	6.52	-0.45
								Mean	6.58	-0.39
								Std. Dev.	0.05	0.05
4	3.49	25.00	13.96	0.50	150.7	109.5	94.8	0.73703	3.26	-0.23
5		25.00	13.96	0.50	150.5	109.4	94.7	0.73656	3.29	-0.20
6		25.00	13.96	0.50	150.6	109.4	94.7	0.73703	3.26	-0.23
								Mean	3.27	-0.22
								Std. Dev.	0.02	0.02
7	0.70	25.00	13.96	0.50	192.1	114.4	97.8	0.82397	0.63	-0.07
8		25.00	13.96	0.50	192.0	114.3	97.7	0.82397	0.63	-0.07
9		25.00	13.96	0.50	191.7	114.3	97.6	0.82253	0.65	-0.05
								Mean	0.64	-0.06
								Std. Dev.	0.01	0.01
10	0.35	25.00	13.96	0.50	209.4	114.9	97.8	0.84677	0.33	-0.02
11		25.00	13.96	0.50	209.3	114.9	97.7	0.84588	0.34	-0.01
12		25.00	13.96	0.50	209.2	114.9	97.7	0.84574	0.34	-0.01
								Mean	0.34	-0.01
								Std. Dev.	0.01	0.01
13	0.07	25.00	13.96	0.50	245.4	115.4	98.1	0.88255	0.08	0.01
14		25.00	13.96	0.50	245.2	115.4	98.1	0.88239	0.08	0.01
15		25.00	13.96	0.50	245.0	115.4	98.1	0.88223	0.08	0.01
								Mean	0.08	0.01
								Std. Dev.	0.00	0.00

highest chloride concentration was  $-0.39 \text{ kg/m}^3$ . Examination of the results for the other four test solutions, presented in Table 1, indicated that the errors appeared to decrease with the concentration of chloride in a solution. In the concentration range of most interest from the standpoint of a corrosion threshold ( $0.07$  to  $0.70 \text{ kg/m}^3$ ), the errors varied from  $-0.06$  to  $0.01 \text{ kg/m}^3$ , which was encouraging. Even more encouraging were the standard deviations for the entire range of concentrations tested, which ranged between  $0.00$  and  $0.05 \text{ kg/m}^3$ . The results clearly demonstrated that the internal calibration method is effective for determining the amount or concentration of chloride ions in an aqueous solution. In fact, the approach should be applicable also to analysis of other ions for which ion-specific electrodes are available.

### Testing on Concrete Samples

The internal calibration technique serves only as a means for determining the amount of chloride ions in a solution that resulted from extraction of these ions from a ground concrete sample. To complete the method, procedures for extracting the chloride ions need to be established, and the critical aspect of any such procedures would be the selection of a solvent with which to treat the ground concrete samples and the treatment or digestion regime. Balancing among interests in keeping the procedures as simple as possible, avoiding the use of

Table 2. Spreadsheet Calculation of Chloride Concentration ( $6.97 \text{ kg/m}^3$ ) in Solution Used in Test 1

Portion	I	J	K	L
1	$C_A \text{ (kg/m}^3\text{)}$	$R_l$	$R_r$	$(R_l - R_r)$
2	1.00	0.68660	0.80407	-0.11747
3	2.00	0.68660	0.76769	-0.08109
4	3.00	0.68660	0.74254	-0.05594
5	4.00	0.68660	0.72309	-0.03649
6	5.00	0.68660	0.70722	-0.02062
7	6.00	0.68660	0.69386	-0.00726
8	6.10	0.68660	0.69263	-0.00603
9	6.20	0.68660	0.69143	-0.00482
10	6.30	0.68660	0.69024	-0.00364
11	6.40	0.68660	0.68907	-0.00246
12	6.50	0.68660	0.68791	-0.00131
13	6.60	0.68660	0.68677	-0.00017
14	6.61	0.68660	0.68666	-0.00006
15	<b>6.615</b>	0.68660	0.68660	<b>0.00000</b>
16	6.62	0.68660	0.68655	0.00006
17	6.64	0.68660	0.68632	0.00028
18	6.66	0.68660	0.68610	0.00051
19	6.70	0.68660	0.68565	0.00095
20	6.80	0.68660	0.68454	0.00206
21	6.90	0.68660	0.68345	0.00315
22	7.00	0.68660	0.68237	0.00423
23	8.00	0.68660	0.67234	0.01427
24	9.00	0.68660	0.66346	0.02314
25	10.00	0.68660	0.65555	0.03106
26	11.00	0.68660	0.64842	0.03818
27	12.00	0.68660	0.64197	0.04464

harsh chemical reagents, and efficiently extracting the chloride ions in each sample, an aqueous solution of acetic acid was chosen as the solvent. The concentration of the acetic acid solution was determined based on the amount of acetic acid that would be needed to neutralize all the cement paste and calcareous aggregates that might be encountered in concrete samples. The procedures eventually established and used in this study on actual chloride-contaminated concrete samples are presented in the Appendix.

To determine the precision of the method when used on concrete samples, several actual concrete samples were divided into 2.5-g portions and each portion was tested using the new procedures.

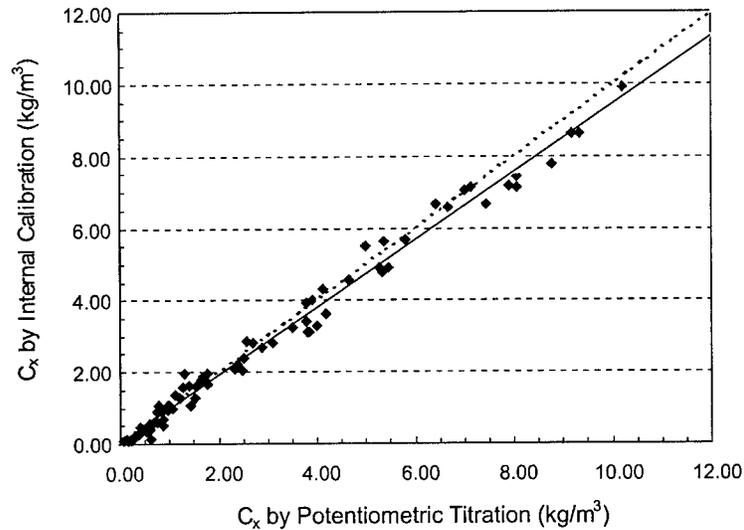
## RESULTS AND DISCUSSION

As the results in Table 3 show, the standard deviations of the tests on concrete samples ranged from 0.05 to 0.30 kg/m<sup>3</sup>, with an average of 0.21 kg/m<sup>3</sup>. Unlike the relatively small standard deviations in testing with the five test chloride solutions, which reflected mostly the expected small fluctuations in potential readings and measurement of the solution volumes, the larger standard deviations with the testing of actual concrete samples reflected additional variations, such as in the chloride contents in different portions of the same sample and the amount of chloride ions extracted into solution. Even so, these standard deviations compared favorably with the 0.10 kg/m<sup>3</sup> suggested for ASTM C-1152 as the limit for a difference between results from two tests.

For comparison with the standard method, numerous concrete samples were analyzed using both the standard method and the method presented here. Figure 2 compares the chloride concentrations of these samples determined by these two methods. Overall, the chloride concentrations measured by the new method averaged about 0.14 kg/m<sup>3</sup> lower than those measured by the standard method. However, the differences averaged only -0.02 kg/m<sup>3</sup> for chloride concentrations between 0.00 to 2.00 kg/m<sup>3</sup>, which is the concentration range of most interest from the standpoint that the most widely accepted corrosion threshold is 0.78 kg/m<sup>3</sup> and the point at which critical decisions on whether mitigation measures need to be applied are made.

Table 3. Precision of Internal Calibration Method

Chloride Contents of Concrete Samples (kg/m <sup>3</sup> )					
Portion	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
1	2.18	3.06	4.76	3.21	1.07
2	2.48	3.50	4.91	3.25	0.99
3	2.18	3.13	4.73	3.78	1.07
4	2.18	3.09	4.38	3.04	1.05
5	2.07	3.27		3.22	1.03
6	2.48	3.14		3.35	1.10
7	2.54	2.96		2.73	1.12
8	2.60	3.54		3.61	0.97
9	2.66	3.49		2.95	
10	2.54	3.27		3.25	
Range	0.59	0.58	0.53	0.83	0.15
Mean	2.39	3.18	4.69	3.24	1.05
Std. Dev.	0.21	0.28	0.22	0.30	0.05



**Figure 2. Comparison of Chloride Concentrations in Different Concrete Samples as Determined by Standard Potentiometric Titration Method and New Method**

The correlation between the magnitude of the differences between the two methods and the chloride concentrations in the concrete samples is reflected in the errors in the testing of the five chloride solutions discussed previously. Such differences appeared to be systematic. This means that the new method can still be improved significantly, perhaps by optimizing part of the procedures, specifically the concentration ( $C_S$ ) and the volume ( $V_S$ ) of the standard NaCl solution used. The values of these two critical factors have not yet been optimized. At its present stage, the new method still has room for improvement.

Similar to the commercial test kits, this new method provides significant advantages over the standard method. First, the procedures, as shown in the Appendix, are significantly shorter and simpler than those in the standard method. Therefore, a sample can be tested in approximately 10 to 15 min, in comparison to a minimum of 45 min for the standard method (if only 12 to 15 samples are analyzed side-by-side per day). This translates into a time savings of at least 75 percent. From the standpoint of reagents, the new method does not require the use of silver nitrate, nitric acid and, occasionally, sodium chloride as the standard method requires; instead, it requires acetic acid and sodium chloride. In terms of the costs of these reagents, the new method costs approximately \$0.16 per sample, which is about \$0.22 less than that needed for the standard method. The costs of the reagents are really not much for either method, so the difference between them is insignificant. However, there is a large difference in the indirect cost associated with the use of silver nitrate in the standard method that is difficult to estimate. This reagent must be stored properly and its disposal after use requires extra care and handling since it is considered potentially hazardous to human health and the environment. If only labor and reagent costs are considered, the new method is cheaper by at least 75 percent.

## CONCLUSIONS

- *The internal calibration method can be used to determine the concentration of chloride ions and any other ion for which an appropriate ion-specific electrode is available. The method appeared to yield lower chloride concentrations than the known concentrations in the test solutions or the concentrations of the concrete samples analyzed by the standard method, depending on the case. However, for actual concrete samples, this difference is relatively insignificant in the low chloride concentration range that is most critical from the standpoint of the widely accepted corrosion threshold. In any case, the difference or deficiency, depending on one's perspective, can be eliminated with additional optimization of particular parameters in the new procedure.*
- *This new method costs considerably less than the standard method because of the direct savings in the time and reagents required and the indirect savings in eliminating the need to use silver nitrate, which is a potentially hazardous reagent that requires proper handling during use and disposal after use.*

## RECOMMENDATION

- *VDOT should begin using the new method developed in this study, side-by-side with the standard method, until sufficient experience is gained to allow a determination of whether to adopt its use.*

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## APPENDIX

### An Internal-Calibration Potentiometric Method for Determining the Chloride Ion Content in Ground Concrete Samples

#### 1. Scope

1.1 The procedures given do not cover the collection of concrete samples from a structure, which is adequately described in AASHTO T-260.

#### 2. Reagents

- 2.1 Distilled water.
- 2.2 Sodium chloride, NaCl, reagent grade.
- 2.3 Glacial acetic acid.
- 2.4 Ionic-strength adjustor.
- 2.5 Standard 1.000 M NaCl solution. Dry reagent grade NaCl in an oven at 105°C. Cool in a desiccator. Weigh out 58.444 grams, dissolve in distilled water, and transfer to a 1-liter volumetric flask. Dilute with additional distilled water to bring to mark. Mix thoroughly.
- 2.6 1.75M Acetic acid solution. Dilute 100 mL of glacial acetic acid in a 1-liter volumetric flask with sufficient amount of distilled water to bring the solution up to mark.

#### 3. Apparatus

- 3.1 Combination chloride-ion selective electrode.
- 3.2 pH/mV meter, with accuracy of  $\pm 0.1$  mV and resolution of 0.1 mV, and input for an automatic temperature compensation probe.
- 3.3 Automatic temperature compensating (ATC) probe, compatible with the pH/mV meter.
- 3.4 Balance sensitive to 0.0001 gram with a minimum capacity of 100 grams.
- 3.5 An adjustable-volume digital pipetter, with a range of 0.200 to 1.000 mL.
- 3.6 Glassware: 150-mL beakers, 5-mL and 50-mL graduated cylinders.
- 2.7 Magnetic stirrer and Teflon-coated stirring bars.

#### 4. Procedure

- 4.1 Weigh to the nearest milligram a 2.5-gram powdered sample representative of the concrete under test. Record the weight as  $W_{sample}$ .
- 4.2 Place a stirring bar in a 150-mil beaker, and transfer the sample quantitatively into the beaker.
- 4.3 Measure 50 mL of the acetic acid solution and carefully transfer into the beaker. Stir the solution gently for few minutes with the magnetic stirrer. Then, let the solution cool to room temperature if necessary.
- 4.4 Add 2.0 mL of ionic-strength adjustor.

- 4.5 Immerse the tips of the combination chloride-ion electrode and the ATC probe in the solution without disturbing the stirring. Record the new potential reading as  $E_x$ . Keep the solution continuously stirred.
- 4.6 Add 0.50 mL of the standard 1.000M NaCl solution with a digital pipetter, and record the new potential as  $E_{x+S}$ .
- 4.7 Add a second 0.50 mL of the standard 1.000M NaCl solution and record the final potential reading as  $E_{x+2S}$ . Stop the stirring of the solution.
- 4.8 Calculate the chloride content of sample with the following spreadsheet.

### Spreadsheet for Calculation of $C_x$

This portion is for entry of the weight of each sample used and the measured potentials, before and after each addition of a 0.50-mL portion of a standard 1.000M NaCl solution.

A	B	C	D	E	F	G	H
1	Sample No.	$C_s$ (kg/m <sup>3</sup> )	$E_x$ (mV)	$E_{x+s}$ (mV)	$E_{x+2s}$ (mV)	$C_x$ (kg/m <sup>3</sup> )	1
2		$= (0.01773 * 100 / B2) * 23.60$					2
3		$= (0.01773 * 100 / B3) * 23.60$					3
4							4
5							5
6							6
7							7

This portion performs the iterative calculation to arrive at the  $C_x$  of each sample:

I	J	K	L
1	$C_A$ (kg/m <sup>3</sup> )	$R_i$	$(R_i - R_r)$
2	0.10	$= (\$D\$2 - \$E\$2) / (\$D\$2 - \$F\$2)$	=J2-K2
3	0.20	=J2	=J3-K3
4	0.30	=J2	=J4-K4
5	0.40	=J2	=J5-K5
6	0.50	=J2	=J6-K6
7	0.60	=J2	=J7-K7
Etc.	Etc.	Etc.	Etc.

Notes:

- The formula in this column C calculates the equivalent of the amount (0.01773 g) of chloride ions present in 0.50 mL of 1.000M NaCl solution in kg Cl/m<sup>3</sup> of concrete. The factor of 23.60 is for converting % Cl<sup>-</sup> by weight of concrete to kg Cl/m<sup>3</sup> of concrete. This conversion factor is unnecessary, if the unit of % Cl<sup>-</sup> by weight of concrete is preferred.
- The second portion of this spreadsheet is to be used to calculate the chloride content of a concrete sample, one at a time.
- As the rate at which the value of  $(R_i - R_r)$  approaches 0 becomes higher, the increment used in column I can be decreased to 0.01 or even 0.005 or any value in between that is practical.

