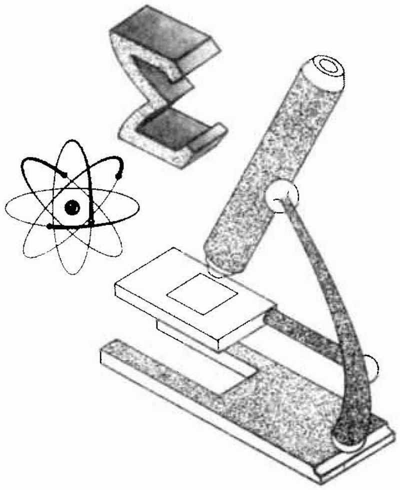
Report No. FHWA-RD-77-85

SAMPLING AND TESTING FOR CHLORIDE ION IN CONCRETE



DEPARTMENT OF TRANSPORTATION ★ UNITED STATES OF AMERICA ★

August 1977

Interim Report

FEDERAL HIGHWAY ADMINISTRATION
Offices of Research & Development
Washington, D. C. 20590

FOREWORD

This report presents recommended methods for sampling and testing for both total and water-soluble chloride ion in hardened concrete. Alternate procedures for sampling the hardened concrete with either a core drill or a rotary impact drill are included. Two alternate methods of chemical analysis are presented, a potentiometric titration method and a significantly more rapid method employing the Gran endpoint determination procedure. Both methods are compatible with either chloride or silver ion-selective electrodes.

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Director, Office of Research

NOTICE

Technical Report Documentation Page

1. Report No.
FHWA-RD-77-85

2. Government Accession No.

3. Recipient's Catalog No.

4. Title and Subtitle
Sampling and Testing for Chloride Ion in Concrete

5. Report Date
August 1977

6. Performing Organization Code

7. Author(s)
K.C. Clear and E.T. Harrigan

8. Performing Organization Report No.

9. Performing Organization Name and Address
Federal Highway Administration
Offices of Research and Development
Materials Division
Washington, D.C. 20590

10. Work Unit No. (TRAIS)
FCP No. 24B1012

11. Contract or Grant No.
Staff Report

12. Sponsoring Agency Name and Address
U. S. Department of Transportation
Federal Highway Administration
Offices of Research and Development
Washington, D.C. 20590

13. Type of Report and Period Covered
Interim Report
February - July 1977

14. Sponsoring Agency Code
M-0401

15. Supplementary Notes
Staff effort related to FCP Project 4B, "Eliminate Premature Deterioration of Portland Cement Concrete"

16. Abstract

One of the most severe problems facing the highway community is chloride ion-induced reinforcing steel corrosion and the subsequent deterioration of concrete bridge decks and marine structures. This report presents recommended methods for sampling and testing for both total and water-soluble chloride ion in hardened concrete. The methods are updated and expanded revisions of the earlier procedure developed by FHWA and contained in report FHWA-RD-72-12, "Determination of Chloride in Hardened Portland Cement Paste, Mortar and Concrete" by H. A. Berman and report FHWA-RD-74-5, "Evaluation of Portland Cement Concrete for Permanent Bridge Deck Repair."

Alternate procedures for sampling the hardened concrete with either a core drill or a rotary impact drill are included. In addition, two alternate methods of chemical analysis are presented, the original potentiometric titration method and a significantly more rapid method employing the Gran endpoint determination procedure. Both are compatible with either chloride or silver ion-selective electrodes.

17. Key Words
Concrete, bridge deck reinforcing steel, corrosion, deicer, chloride ion analysis, repair, rotary impact drill, core drill.

18. Distribution Statement
No restrictions. This document is available through the National Technical Information Service, Springfield, Virginia 22161.

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price
Unclassified	Unclassified	25	

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TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

Figure

LIST OF TABLES

Table

PREFACE

One of the most severe problems facing the highway community is chloride-induced reinforcing steel corrosion and the subsequent deterioration of concrete bridge decks and marine structures. The Federal Highway Administration, Offices of Research and Development, consider the development of methods for the elimination of bridge deck deterioration as one of their highest priority efforts. The problems and the approach to solution of the problems are defined in Project 4B of the Federally Coordinated Program of Research and Development in Highway Transportation under the title, "Eliminate Premature Deterioration of Portland Cement Concrete."

The authors wish to acknowledge the valuable technical assistance of Messrs. Ernest F. Bailey and Douglas D. Simmons who performed the chemical analyses for Part IV of this report and contributed greatly to the formulation of the procedures contained in Parts II and III.

I. INTRODUCTION

During the past several years, the Federal Highway Administration has devoted considerable effort to solving the severe problem of bridge deck damage caused by chloride ion-induced reinforcing steel corrosion (principally as a result of the increasing use of deicing salts).

One of the main areas of investigation has dealt with development of an accurate, reliable method for determining the chloride ion concentration of hardened portland cement concrete (PCC). Such a method is essential in assessing the need and magnitude of maintenance on existing bridge decks, as well as assuring that materials used in new construction do not contain potentially harmful chloride ion levels.

Such an analytical method was developed by Berman[1] and presented in procedural form by Clear[2] in 1974. In the interim this method, which involves dissolution of the PCC by nitric acid and subsequent potentiometric titration of the chloride ion with standard silver nitrate solution, has received wide dissemination by FHWA and is in use by many State highway organizations.

This report contains a complete revision of this original method. This revision was necessitated by two factors. First, continual and large-scale use of the method in the laboratories of FHWA's Materials Division uncovered a number of points in the original method which required elaboration or clarification. Second, a number of new techniques were tried and proven which have considerably simplified the method and significantly reduced the analysis time per sample.

The major change in the method given here is the inclusion of the alternate Gran endpoint determination procedure in addition to the original potentiometric titration procedure. The original application of the Gran procedure to this analysis was made by Clemena, Reynolds and McCormick[3]. Extensive laboratory work by FHWA confirmed the results of the Virginia study, viz., that the Gran procedure applied to this analysis results in a considerable savings in time and labor per determination with no significant change in accuracy and precision from the more laborious original method. The Gran endpoint determination procedure as well as the original method is compatible with both chloride ion and silver ion-selective electrodes, and the methods here allow the use of either of these electrodes. Also, besides an analysis of total chloride, a procedure is included here to determine the concentration of water-soluble chloride ion in a sample. Finally, the revision provides detailed alternate procedures for sampling of the concrete.

Part II of this report contains the complete sampling and testing method for determination of total chloride ion content; the original potentiometric titration procedure is designated as alternate method I while the Gran plot determination procedure is contained in alternate method II. Part III contains the sampling and testing method for water-soluble chloride ion content. Finally, Part IV contains short discussions of the accuracy and repeatability of the methods, the precision between alternate methods I and II, and some data on the measured level of water-soluble chloride ion in typical concrete samples.

II. STANDARD METHOD OF SAMPLING AND TESTING FOR TOTAL CHLORIDE ION IN CONCRETE

1. Scope

1.1 This method covers a procedure for the determination of the total chloride ion content of aggregates, portland cement, mortar or concrete. The method is limited to materials that do not contain sulfides, but the extraction procedure, paragraphs 5.1 thru 5.6, may be used for all such materials.

2. Apparatus

2.1 Samples may be obtained by one of two methods, 2.1.1 or 2.1.2.

2.1.1 Core drill

2.1.2 Rotary impact type drill with a depth indicator and drill or pulverizing bits of sufficient diameter to provide a representative sample of sufficient size for testing.

2.1.2.1 Sample containers capable of maintaining the sample in an uncontaminated state.

2.1.2.2 Spoons of adequate size to collect the sample from the drilled holes.

2.1.2.3 A "blow out" bulb or other suitable means of removing excess pulverized material from the hole prior to re-drilling operations.

2.1.2.4 A pachometer capable of determining the location and depth of steel reinforcement to ± 1/8 inch (± 3mm).

2.2 Testing

2.2.1 Chloride-ion or silver/sulfide ion-selective electrode and manufacturer-recommended filling solutions.

Note: Suggested electrodes are the Orion 96-17 Combination Chloride Electrode or the Orion 94-6 Silver/Sulfide Electrode or equivalents. The Silver/Sulfide electrode requires use of an appropriate reference electrode (Orion 90-02 or equivalent).

2.2.2 A millivoltmeter compatible with the ion electrode.

Note: Suggested millivoltmeter is the Orion Model 701A Digital pH/mv meter or equivalent.

2.2.3 Magnetic stirrer and teflon stirring bars.

2.2.4 Burette with 0.1 ml graduations.

2.2.5 Balance sensitive to 0.0001 gram with minimum capacity of 100 grams.

2.2.6 Balance sensitive to 0.1 gram with minimum capacity of 1 Kg.

2.2.7 Hot plate, 250^0 to 400^0C heating surface temperature.

2.2.8 Glassware - 100 and 250 ml beakers, filter funnels, stirring rods, watch glasses, dropper; mortar and pestle; wash bottles.

2.2.9 Sieve, U.S. Standard 50 mesh.

2.2.10 Whatman No. 40 and No. 41 filter papers (or equivalent).

Note: Filter papers should be checked to confirm they do not contain chloride which will contaminate the sample. If chloride is detected, the papers should be washed with nitric acid and distilled water until no chloride ion is detected.

3. Reagents

3.1 Concentrated HNO_3 (sp. gr. 1.42).

3.2 Sodium chloride, NaCl, reagent grade (primary standard).

3.3 Standard 0.0100 N NaCl solution. Dry reagent grade NaCl in an oven at 105 C. Cool, in a dessicator, weigh out 0.5844 grams, dissolve in distilled H_2O, and transfer to a 1-liter volumetric flask. Make up to the mark with distilled H_2O and mix.

3.4 Standard 0.01 N $AgNO_3$. Weigh 1.7 grams of reagent grade $AgNO_3$, dissolve in distilled H_2O, filter into a 1-liter brown glass bottle, fill, and mix thoroughly. Standardize against 25.00 ml of the NaCl solution by the titration method given in paragraph 5.7.

3.5 Distilled water.

3.6 Methyl orange indicator.

3.7 Ethyl alcohol, technical grade.

4. Method of Sampling

4.1 Determine the depth within the concrete for which the chloride content is desired. Use the pachometer to determine reinforcement bar location and depth. Use of the pachometer is described in references 5a and 5b.

4.2 Core Method - Drill the core to chosen depth and retrieve.

4.2.1 When samples are received in the laboratory in other than pulverized condition, the sample shall be crushed and ground to a powder. All sawing or crushing shall be done dry (i.e. without water). All material shall pass a number 50 mesh sieve. All pulverizing tools and sieves shall be washed with ethyl alcohol or distilled water and shall be dry before use with each separate sample (see note para. 4.3.7).

4.3 Pulverizing Method

4.3.1 Set the rotary hammer depth indicator so that it will drill to 1/4 inch (6 mm) above the desired depth.

4.3.2 Using a drill or pulverizing bit, drill until the depth indicator seats itself on the concrete surface.

4.3.3 Thoroughly clean the drilled hole and surrounding area utilizing the "blow out" bulb or other suitable means.

4.3.4 Reset the depth indicator to permit 1/2 inch (13 mm) additional drilling.

4.3.5 Pulverize the concrete until the depth indicator again seats itself on the concrete.

Note: Care must be exercised during this pulverizing operation to prevent the drill bit from abrading concrete from the sides of the hole above the sampling depth. To prevent this, some users utilize an 0.25 inch (6mm) smaller diameter bit in this step than that used in para. 4.3.2.

4.3.6 Collect at least 10 grams of the material remaining in the hole using a spoon and place in the sample container.

4.3.7 If the sample, as collected, does not completely pass a 50 mesh screen, additional pulverizing shall be performed until the entire sample is finer than 50 mesh.

Note: During sample collection and pulverizing, personnel shall use caution to prevent contact of the sample with hands, or other sources of body perspiration or contamination. Further, all sampling tools (drill bits, spoons, bottles, sieves, etc.) shall be washed with ethyl alcohol or distilled water and shall be dry prior to use on each separate sample. Ethyl alcohol is normally preferred for washing because of the rapid drying which naturally occurs.

5. Procedure

5.1 Weigh to the nearest milligram a 3 gram powdered sample representative of the material under test.

Note: Some users dry the sample to constant weight in a 105°C oven and determine the dry sample weight prior to analysis. This optional procedure provides a constant base for comparison of all results by eliminating moisture content as a variable. It is generally believed that drying is only necessary when very high accuracy is desired (see Reference 2 for data in this area).

Note: Running of blank determinations is recommended to allow correction for any extraneous sources of chloride ion. However, such corrections should be extremely small; large blank corrections indicate sources of contamination which should be eliminated.

Transfer the sample quantitatively to a mortar; add 10 ml of hot ($90^o$to 100^oC) distilled H 0 to the mortar, swirling to bring the powder into suspension. Carefully grind the slurry with a pestle until all lumps are gone. Very little grinding will be necessary for soft aggregates, but considerable effort will be required for samples containing hard aggregates.

Note: Sample particle size after grinding should be such that it will pass a 100 mesh screen. Further, about 75 percent of a properly ground sample will pass a 200 mesh screen. It is suggested that the analyst grind several trial samples, in accordance with the above procedure and then dry the samples and determine the particle size as a means of defining the grinding required for actual samples.

5.2 Transfer the slurry quantitatively from the mortar through a funnel into a 100 ml beaker, rinsing the funnel lightly with hot distilled H_2O. Add 3 ml concentrated HNO_3 to the mortar and stir with the pestle to completely dissolve any cement left in the mortar. Transfer the contents of the mortar through the funnel while continuously stirring the beaker with a glass stirring rod. Rinse the mortar, pestle, inside of the funnel and the tip of the funnel with hot distilled H_2O.

Note: Too rapid transfer of the acid into the 100 ml beaker will cause excessive foaming or frothing of samples with calcareous aggregates or organic components and resultant risk of sample loss.

5.3 Make up the solution in the 100 ml beaker to approximately 50 ml with hot distilled H_2O. Stir thoroughly to ensure complete sample digestion. Add five drops of methyl orange indicator and stir. If yellow to yellow-orange color appears, the solution is not sufficiently acidic. Add additional concentrated HNO_3 dropwise with continuous stirring until a faint pink or red color persists in the solution. Cover with a watch glass, retaining the stirring rod in the beaker.

Note: Due to the presence of relatively insoluble materials in the sample, the solution generally will have a strong gray color, making the detection of the indicator color difficult at times. Running of several trial samples is suggested to give the analyst practice in detecting the indicator color.

5.4 Bring the solution in the covered 100 ml beaker to a boil on a medium heat (250°to 400°C) hot plate, and then boil for a full minute with care to avoid frothing and spillovers. Remove from heat.

Note: The analysis can be stopped at this point and the sample allowed to cool in an HCl fume-free area if it is necessary. Before proceeding to the next step, however, the solution must again be brought to a boil.

5.5 Prepare a funnel fitted with double filter paper (Whatman No. 41 over No. 40 filter paper or equivalents) and a 250 ml beaker to receive the filtrate. Carefully lift the watch glass from the 100 ml beaker, without tilting it, and wash any adhering drops into the filter paper with hot distilled water. Then filter the hot solution into the 250 ml beaker. Proceed carefully, employing the stirring rod to aid quantitative transfer of the solution into the filter funnel. Wash the inside of the 100 ml beaker and the stirring rod twice with hot distilled H_2O. Transfer the washings through the filter into the 250 ml beaker. Finally, carefully wash the outside of the pouring lip of the 100 ml beaker with hot distilled H_2O into the filter.

5.6 Wash the filter paper five to ten times with hot distilled H_2O, being careful not to lift the paper away from the funnel surface. Finally, lift the filter paper carefully from the funnel and wash the outside surface of the paper with hot distilled H_2O; then wash the tip of the funnel. The final volume of the filtered solution should be 125 to 150 ml. Cover with a watch glass and allow to cool to room temperature in an HCl fume-free atmosphere.

5.7 Two alternate methods are available to determine the Cl^- content of the solution. Both methods utilize an ion-selective electrode (Cl^- or $Ag+$) and both methods for the purpose of this analysis give results of essentially equal accuracy and precision. However, Method II offers a substantial decrease in time required for analysis over Method I.

5.7.1 Alternate Method I: Potentiometric Titration

Fill the Cl^- or the $Ag+$ electrode with the solution(s) recommended by the manufacturer, plug it into the millivoltmeter (preferably the type with a digital rather than a dial readout), and determine the approximate equivalence point by immersing the electrode in a beaker of distilled H_2O. Note the approximate millivoltmeter reading (which may be unsteady in H_2O).

Take the cooled sample beaker from 5.6 and carefully add 4.00 ml of 0.01 N NaCl, swirling gently. Remove the beaker of distilled H_2O from the electrode, wipe the electrode with absorbent paper, and immerse the electrode in the sample solution. Place the entire beaker-electrode assembly on a magnetic stirrer and begin gentle stirring.

Using a calibrated buret, add gradually and record the amount of standard 0.01 N $AgNO_3$ solution necessary to bring the millivoltmeter reading to - 40 mv of the equivalence point determined in distilled H_2O. Then add standard 0.01N $AgNO_3$ solution in 0.10 ml increments recording the millivoltmeter reading after each addition.

As the equivalence point is approached, the equal additions of $AgNO_3$ solution will cause larger and larger changes in the millivoltmeter reading. Past the equivalence point, the changes per unit volume will again decrease. Continue the titration until the millivoltmeter reading is at least 40 mv past the approximate equivalence point.

The endpoint of the titration usually is near the approximate equivalence point in distilled water and may be determined by (1) plotting the volume of $AgNO_3$ solution added versus the millivoltmeter readings. The endpoint will correspond to the point of inflection of the resultant smooth curve, or (2) calculating the differences in millivoltmeter readings between successive $AgNO_3$ additions and calculating the total volume of $AgNO_3$ which corresponds with each difference (i.e., the midpoints between successive additions).

Example:

Raw Data		Differences	
Titrant Volume	Millivolt Reading	Titrant Midpoints	Millivolt Differences
4.2 ml	130.0	4.25 ml	5.0
4.3 ml	135.0	4.35 ml	7.0
4.4 ml	142.0	4.45 ml	10.0
4.5 ml	152.0	etc.	
etc.			

The endpoint will be near the midpoint which produced the largest change in millivoltmeter reading. It may be determined by plotting midpoints versus differences and defining the $AgNO_3$ volume which corresponds to the maximum difference on a smooth, symmetrical curve drawn through the points. However, it can usually be estimated accurately without plotting the curve by choosing the midpoint which corresponds to the maximum difference and adjusting for asymmetry, if any. In other words, if the differences on each side of the largest difference are not symmetrical, adjust the endpoint mathematically in the direction of the larger differences. Detailed examples of this adjustment are presented in Figures 1 and 2; further discussion is contained in Reference 2.

5.7.2 Alternate Method II: Gran Plot Method

This method is compatible with either a Cl^- or $Ag+$ ion-selective electrode. Attach the electrode of choice to a compatible digital millivoltmeter after filling with required solutions as per the electrode manufacturer's instructions. Clean the electrode with distilled H_2O and pat dry with absorbent paper.

Ml. $AgNO_3$ added	Reading mv.	Difference mv.
0.0	36.1	
		10.8
5.0	46.9	
		8.6
8.0	55.5	
		12.2
11.0	67.7	
		12.4
13.0	80.1	
		9.0
14.0	89.1	
		6.3
14.5	95.4	
		7.7
15.0	103.1	
		11.8
15.5	114.9	
		6.2
15.7	121.1	
		8.7
15.9	129.8	
		5.1
16.0	134.9	
		6.9
16.1	141.8	
		8.2
16.2	150.0	
		10.5
16.3	160.5	
16.35 END POINT		12.0
16.4	172.5	
		10.7
16.5	183.2	
		8.9
16.6	192.1	
		6.8
16.7	198.9	
		5.6
16.8	204.5	

SYMMETRICAL REGION

Figure 1. A typical symmetrical chloride titration.

Symmetrical, 2 High Differences

ml. AgNO$_3$ added	Reading mv.	Diff. mv.
25.2	146.7	
		7.8
25.3	154.5	
		8.9
25.4	163.4	
		10.8
25.5	174.2	
		10.8
25.6	185.0	
		8.5
25.7	193.5	
		7.5
25.8	201.0	

ENDPOINT = 25.50

Unsymmetrical, small skew

ml. AgNO$_3$ added	Reading mv.	Diff. mv.
11.8	140.8	
		9.8
11.9	150.6	
		12.3
12.0	162.9	
		14.6
12.1	177.5	
		14.0
12.2	191.5	
		10.1
12.3	201.6	
		8.0
12.4	209.6	
		6.1
12.5	215.7	

ENDPOINT = 12.09

Unsymmetrical, half-way skew

ml. AgNO$_3$ added	Reading mv.	Diff. mv.
14.1	138.0	
		8.0
14.2	146.0	
		9.4
14.3	155.4	
		12.4
14.4	167.8	
		12.3
14.5	180.1	
		11.0
14.6	191.1	
		8.1
14.7	199.9	
		6.0
14.8	205.9	

14.45
- .02
14.43

14.40
+ .02
14.42

ENDPOINT
AVERAGE = 14.425

Unsymmetrical, large skew

ml. AgNO$_3$ added	Reading mv.	Diff. mv.
7.1	139.1	
		7.3
7.2	146.4	
		9.7
7.3	156.1	
		11.3
7.4	167.4	
		12.1
7.5	179.5	
		10.5
7.6	190.0	
		8.0
7.7	198.0	
		6.4
7.8	204.4	
		5.0
7.9	209.4	

7.45
-.02
7.43

ENDPOINT = 7.43

Figure 2. Other types of endpoint regions.

Weigh the cooled sample and beaker from 5.6 without the watch glass and record the weight. Using a calibrated buret, titrate the sample to 225 mv $\pm$ 5 mv (Cl^- electrode) or 310 $\pm$ 5 mv (Ag^+ electrode) with standard 0.01N $AgNO_3$ solution. Record the volume added and the millivoltmeter reading.

Continue to titrate in 0.50 ml increments recording the volume added and the millivoltmeter reading for each increment. Add and record the data for at least five increments. Empty, clean, dry and weigh the beaker. Subtract beaker weight from beaker + solution weight determined above to define solution weight.

Additional information on the Gran Method is given in Reference 3.

6. Calculations

6.1 Alternate Method I - Potentiometric Titration

Determine the endpoint of the titration as described in para. 5.7.1 by either plotting a curve or estimating from the numerical data. Calculate the percent Cl^- ion from the equation:

$$\%Cl^- = 3.5453 \frac{(V_1 N_1 - V_2 N_2)}{W}$$

Where V_1 = endpoint in ml V_2 = Volume of NaCl solution added, in ml

N_1 = normality of $AgNO_3$ N_2 = Normality of NaCl Solution

W = Weight of original concrete sample in grams

6.2 Alternate Method II - Gran Plot Method

Calculate corrected values for each of the volumes recorded in 5.7.2 by the equation:

$$V_{correct} = \frac{V_{record}}{W/100}$$

Where W = original solution weight in grams

V record = Volumes recorded in ml

If any of the V correct values are greater than 10, see para. 6.3. If less than 10, plot these corrected values versus the corresponding millivolt readings on Orion Gran Plot Paper (10 percent volume corrected type with each major vertical scale division equal to 5 millivolts) or equivalent. Draw the best straight line through the points and read the endpoint at the intersection of the line with the horizontal axis of the graph. Calculate the actual endpoint by the equation:

$$E_a \text{, ACTUAL ENDPOINT} = E_g \frac{W}{100}$$

where E_g= Endpoint determined from graph in ml

W = Weight of solution in grams

Then $\% \text{ Cl} = \frac{3.5453}{W_c} E_a N$

Where E_a = Actual endpoint, in ml; N = Normality of $AgNO_3$ solution and
W_c = Concrete sample weight in grams

6.3 Supplementary Gran Method Calculations:

When the V correct volumes determined in 6.2 are greater than 10, discard the values and follow the following procedure.

Choose a constant which, when subtracted from all V record volumes, yields values less than 10 ml.

Note: This constant, designated as X in the formulas below, is normally assigned an even value such as 5, 10, 15, 20, etc.

Calculate a revised solution weight W_r as

$$Wr = W + X$$

where W = original solution weight in grams
X = the constant

Then calculate corrected volumes for each recorded volume as:

$$V \text{ correct} = \frac{V \text{ record} - X}{W_r/100}$$

Plot these values and determine the graph endpoint E_g as described in para. 6.2. The actual endpoint, E_a is then:

$$E_a = E_g \left(\frac{W_r}{100}\right) + X$$

where E_a = actual endpoint in ml

E_g = endpoint from graph in ml

W_r = revised solution weight in grams

X = the constant chosen above.

Calculate the chloride content using the formula given in para. 6.2.

6.4 The percent chloride may be converted to pounds of Cl^- per cubic yard of concrete as follows:

$$\text{lbs } Cl^-/yd^3 = \% \text{ Cl} \left(\frac{UW}{100}\right)$$

Where

UW = Unit weight of concrete per cubic yard.

Note: A unit weight of 3915 lbs/yd^3 is often assumed for normal structural weight concrete when the actual unit weight is unknown.

III. STANDARD METHOD OF TESTING FOR WATER-SOLUBLE CHLORIDE ION IN CONCRETE

1. Scope

1.1 This method covers a procedure for the determination of the water soluble chloride ion content of aggregates, portland cement, mortar or concrete. The method is limited to materials that do not contain sulfides, but the extraction procedure, paragraphs 5.1 thru 5.6, may be used for all such materials.

1.2 This method is similar to Section II, "Standard Method of Testing for Total Chloride Ion in Concrete," except that a boiling water extraction procedure is used rather than a nitric acid extraction. Consequently, Paragraphs 2, 3, 4, 5.1, 5.7 and 6 of Section II are applicable while paragraphs 5.2 thru 5.6 are not.

1.3 The age of concrete, mortar, or hydrated portland cement at the time of sampling will have an affect on the water soluble chloride content. Therefore, unless early age studies are desired, it is recommended that the material be well cured and at least 28 days of age before sampling.

Procedure:

Follow paragraphs 2, 3, 4, 5.1, 5.7 and 6 of Section II, "Standard Method of Testing for Total Chloride Ion in Concrete,"

Substitute the following for paragraphs 5.2 thru 5.6 of the above referenced total chloride method.

5.2 Transfer the ground sample quantitatively from the mortar through a funnel into a 100 ml beaker. Wash mortar and pestle at least four times each with approximately 5 ml units of hot distilled H_2O. Finally wash the funnel with hot distilled H_2O. Final volume should be 60-70 ml.

5.3 Cover the beaker with a watch glass and bring to a boil on a magnetic stirrer using a small magnet. Boil for 5 minutes, then let stand for 24 hours from the end of the boil in an atmosphere free of HCl fumes.

5.4 Prepare a funnel fitted with a double filter paper (Whatman No. 41 over No. 40 filter paper or equivalent) and a 250 ml beaker to receive the filtrate. Lift the watch glass from the 100 ml beaker and wash any adhering drops into the filter paper. Carefully decant the clear supernatant liquid into the filter paper using a stirring rod to aid transfer.

5.5 Add sufficient hot distilled H_2O to cover the residue in the 100 ml beaker, stir 1 minute on a magnetic stirrer and pour the mixture into the filter paper while swirling the beaker. Wash the inside of the beaker and the stirring rod once into the filter using hot distilled H_2O. Set aside the beaker and stirring rod without further washing. Wash the filter paper <u>once</u> with hot distilled H_2O.

Lift the filter paper carefully from the funnel and wash the outside of the paper with hot distilled H_2O. Set aside the paper and wash the interior of the funnel and its tip with hot distilled H_2O.

5.6 Add 1-2 drops of methyl orange indicator to the 250 ml beaker; then add concentrated HNO_3 dropwise with continuous stirring until a permanent pink to red color is obtained. Make up the volume to 125 to 150 ml.

IV. DISCUSSION

Accuracy and Repeatability of the Analytical Methods

In any chemical analysis the accuracy and repeatability of the method used is of prime importance to the analyst. This is particularly true of the methods for chloride analysis presented in Sections II and III of this report since decisions involving the expenditure of substantial funds are made based on the results obtained.

The accuracy of a chemical analysis is defined as the difference between the measured value of the substance analysed and its true value. The accuracy of the general method in Sections II and III was measured by Berman (1) using portland cement paste specimens to which specific quantities of chloride ion had been added. He found that the accuracy of the method was within 0.5 percent of the total chloride present. For a paste with 1.0 lb Cl^-/yd^3 (.592 kg/m^3) or 0.0255 percent Cl^- by weight, 0.5 percent would be 0.005 lb Cl^-/yd^3 (.00296 kg/m^3) or 0.0001 percent Cl-by weight.

Clemena, Reynolds, and McCormick (2) investigated the accuracy of this method, as well as atomic absorption and neutron activation analysis procedures, for separate series of concrete samples containing siliceous and carbonaceous aggregates with known quantities of added chloride ion. Each series also contained a blank with no chloride added. Based on multiplicate analyses for each specimen, the authors found that for the potentiometric titration method the average accuracy was 3.4 percent of the total chloride present, representing a range of errors from zero to 8.2 percent respectively for specimens with chloride contents between .95 and .39 lbs Cl^-/yd^3 (.560 and .238 kg Cl^-/m^3) (based on a unit weight for concrete of 3915 lbs/yd^3(2318 kg/m^3). For siliceous aggregates, the average accuracy was 3.7 percent and for carbonaceous aggregates, 3.1 percent. These accuracies were considerably better than those obtained by either neutron activation or atomic absorption techniques.

When the analyst deals with actual unknown samples, the accuracy cannot be determined. In this case, which, of course, corresponds to the routine, day-to-day situation, the exactness of a measurement is expressed in terms of the repeatability and precision of the results. Using the potentiometric titration procedure (Method I), Lankard, Moreland, et al (4) at Battelle Memorial Institute performed repeatability tests on 10 specimens of portland cement concrete, each of which was split into four samples. The results are shown in Table 1. The maximum difference between any of the four samples taken from a single specimen was 0.19 lb Cl^-/yd^3 (0.0048 percent $Cl^-$by weight); the average maximum difference was 0.10 lb Cl^-/yd^3 (0.0026 percent $Cl^-$by weight).

Similar tests have been performed in the FHWA laboratory. Table 3 compares analyses performed 1 year apart on the same field samples by different operators. Table 4 presents the results of analyses of low chloride content samples by different operators and different methods; for run 1 the potentiometric titration method (alternate method I) was used while for run 2 the Gran plot method (alternate method II) was used. If we define the precision of the measurements as the absolute deviation of the measurement divided by the arithmetical mean of the measurements expressed as a percentage, we find that the worst precision obtained is 22 percent, representing a deviation from the mean of .115 lbs Cl^-yd^3 (.068 kg Cl^-/m^3) or .0029 percent Cl^- by weight. Such variation on a practical level is not considered significant.

The data in Tables 1-4 are concerned with the analysis for total chloride ion content in a sample (Section II). Repeatability data was also gathered on the procedure for determining water soluble chloride ion content (Section III). These results are presented in Table 5 for samples with a variety of chloride ion contents. Maximum precision as defined above was 33 percent for a sample (#3) with a mean chloride ion content of .06 lbs/yd^3 (.04 kg/m^3) or .0015 percent by weight. Again, such a deviation has no practical significance. For sample 1 with a mean chloride ion content of 4.87 lbs/yd^3 (2.88 kg/m^3) the precision was 1.02 percent or .05 lbs Cl^-/yd^3 (.03 kg Cl^-/m^3) (.0013 percent Cl^- by weight).

In summary, the analytical procedures presented in sections II and III of this report have demonstrated accuracies, repeatability and precisions which are satisfactory for the purpose the analyses are designed to fulfill.

Soluble versus Total Chloride Ion Content in Concrete

To provide insight into the water-soluble and total chloride ion contents of concrete measured using the FHWA analytical methods in Sections II and III, 45 concrete samples were studied. Each sample had a cement content of 658 lbs/yd^3 (389 kg/m^3); the samples were obtained at various depths within large slabs using the rotary hammer sampling procedure. All chloride ion present in these concretes was due to the ponding of NaCl after the concrete was 6 weeks of age; no chloride ion was deliberately mixed into the fresh concrete. Baseline (before salting) total chloride ion content was 0.3 to 0.4 lbs/yd^3 (.2 kg/m^3) (0.045 to 0.061 percent Cl^- by weight of cement). The type I cement used in all concrete had a free lime (CaO) content of 1.12 percent and the concrete age when sampled was 3 years. Table 6 presents the results of the analyses. The percentage of soluble chloride ion in the total generally decreased as the total chloride ion content decreased. This is consistent with the expectation that the soluble chloride ion is due predominantly to intrusion of the ponding solution while the insoluble chloride content mainly arises from the original cement and aggregate composition.

Comparison of Total Chloride Ion Analysis by Methods I and II

Table 7 contains a comparison of the results of the total chloride ion analysis of identical samples by the potentiometric titration procedure (Alternate Method I) and the Gran plot procedure (Alternate Method II) contained in Section II. Both chloride and silver ion-selective electrodes were used. Review of the data shows that the inter-method precision is essentially equal for a variety of concrete types and chloride ion concentrations.

Table 1. Repeatability of chloride determinations on portland cement concrete

Specimen No.	Total Chloride Content, lbs Cl^-/yd^3 Sample 1	Sample 2	Sample 3	Sample 4	Range (Maximum difference) lbs Cl^-/yd^3
1	5.65	5.61	5.73	5.69	0.12
2	5.22	5.18	5.37	5.22	0.19
3	4.71	4.75	4.82	4.67	0.15
4	4.47	4.59	4.31	4.47	0.16
5	2.39	2.39	2.35	2.31	0.08
6	2.27	2.31	2.24	2.31	0.07
7	1.02	0.94	0.98	0.94	0.08
8	0.94	0.94	0.94	0.94	0.00
9	0.75	0.71	0.78	.078	0.07
10	0.67	0.67	0.63	.067	0.04
				Average	0.10

$1b/yd^3 = .592\ kg/m^3$

1/ 1-inch (25.4 mm) thick, 4-inch (101.6 mm) diameter concrete sections which were pulverized and split into four parts. A 10-gram sample was then obtained from each part.

Table 2. Repeatability tests using different operators

Specimen No.	Sample No.	Total Chloride Content (lbs Cl^-/yd^3) Operator 1	Operator 2
1	1	1.55	
	2		1.56
	3	1.59	
	4		1.62

Maximum difference = 0.07 lbs Cl^-/yd^3

Specimen No.	Sample No.	Operator 1	Operator 2
2	1	1.53	
	2		1.44
	3	1.51	
	4		1.50
	5	1.50	
	6		1.48

Maximum difference = 0.09 lbs Cl^-/yd^3

$1b/yd^3 = 0.592\ kg/m^3$

Table 3. Repeatability tests on field samples [1/]

Sample No.	Total Cl^- content, lbs/yd ^{3} Run 1 (1975)	Run 2 (1976)	Difference
3171	2.23	2.28	0.05
3182	0.47	0.59	0.12
3279	2.78	2.75	0.03
3283	2.94	2.93	0.01
3284	0.63	0.73	0.10
3291	1.68	1.72	0.04
3323	3.80	3.93	0.13
3324	0.82	0.82	0.00

lb/yd^3 = 0.592 kg/m^3

[1/] Analyses were performed 1 year apart by the same laboratory but different operators using the potentiometric titration method and a chloride ion-selective electrode.

Table 4, Repeatability Tests on Low Chloride Content Samples [1/]

Sample No.	Total Cl^- content, lbs/yd ^{3} Run 1	Run 2	Difference
1	0.27	0.31	0.04
2	0.47	0.47	0.00
3	0.74	0.55	0.19
4	0.90	0.90	0.00
5	0.67	0.43	0.23
6	0.19	0.21	0.02
7	0.33	0.27	0.06
8	0.28	0.28	0.00
9	0.31	0.25	0.06
10	0.32	0.24	0.08
11	0.36	0.38	0.02
12	0.39	0.30	0.09
13	0.34	0.30	0.04
14	0.32	0.40	0.08
15	0.23	0.21	0.02
16	0.25	0.32	0.07

lb/yd^3= 0.592 kg/m^3

[1/] These runs were made 6 weeks apart by different operators using different titrant solutions. Run 1 used the potentiometric titration method, while Run 2 used the Gran plot method. All analyses were made with a chloride ion-selective electrode.

Table 5. Repeatability Tests for water-soluble chloride content[1/]

Sample No.	Water-soluble Cl^- content, lbs/yd^3 Run 1	Run 2	Difference
1	4.82	4.92	0.10
2	1.37	1.35	0.02
3	0.04	0.08	0.04
4	1.72	1.76	0.04
5	0.30	0.22	0.08

lb/yd^3 = 0.592 kg/m^3

[1/] All analyses were made using the Gran plot procedure with a chloride ion-selective electrode.

Table 6. Water Soluble and Total Chloride Contents

Sample No.	Chloride content, lbs/yd^3		Difference 1/	%Soluble Chloride
	Soluble	Total		
1	25.9	28.8	2.9	90
2	25.9	28.2	2.3	92
3	18.3	20.5	2.2	89
4	16.7	18.1	1.40	92
5	12.9	13.4	0.5	96
6	8.30	9.06	0.76	92
7	4.82	5.32	0.50	91
8	3.01	3.41	0.40	88
9	2.94	3.39	0.45	87
10	2.46	2.95	0.49	83
11	2.43	2.86	0.43	85
12	1.97	2.42	0.45	81
13	1.97	2.47	0.50	80
14	1.95	2.44	0.49	80
15	1.72	1.92	0.20	90
16	1.57	1.90	0.33	83
17	1.48	1.79	0.31	83
18	1.44	1.76	0.32	82
19	1.41	1.84	0.43	77
20	1.37	1.51	0.14	91
21	1.25	1.52	0.27	82
22	1.15	1.48	0.33	78
23	0.95	1.18	0.23	81
24	0.81	1.06	0.25	76
25	0.78	0.97	0.19	80
26	0.73	0.93	0.20	78
27	0.66	0.86	0.20	77
28	0.64	0.92	0.28	70
29	0.51	0.70	0.19	73
30	0.39	0.57	0.18	68
31	0.35	0.56	0.21	63
32	0.34	0.55	0.21	62
33	0.31	0.49	0.18	63
34	0.30	0.47	0.17	64
35	0.29	0.39	0.10	74
36	0.26	0.45	0.19	58
37	0.23	0.36	0.13	64
38	0.22	0.31	0.09	71
39	0.22	0.35	0.13	63
40	0.19	0.35	0.16	54
41	0.17	0.46	0.29	37
42	0.16	0.47	0.31	34
43	0.16	0.43	0.27	37
44	0.15	0.39	0.24	38
45	0.08	0.29	0.21	28

lb/yd^3 = 0.592 kg/m^3

1/ Total chloride minus soluble chloride

To convert lbs/yd^3 to percent by weight of concrete divide by 39.15.
To convert lbs/yd^3 to percent by weight of <u>cement</u> multiply by 0.152.

Table 7. Comparison of Chloride Ion Analysis Alternate Method I and II

Concrete Type/ Sample No.	% Cl^- Method I 1/	% Cl^- Method II 2/	Difference (II - I)	% Difference (II - I/I)	% Cl^- Method II 3/	Difference (II - I)	% Difference (II - I/I)
Conventional Concrete/							
5208	0.117	0.117	0	0	0.119	+.002	1.7
5210	0.098	0.094	-.004	4.1	0.098	0	0
5212	0.102	0.101	-.001	1.0	0.103	+.001	1.0
5175	0.042	0.042	0	0	0.043	+.001	2.4
5176	0.297	0.298	+.001	0.3	0.296	-.001	0.3
5177	0.410	0.400	-.010	2.4	0.410	0	0
5178	0.091	0.091	0	0	0.094	+.003	3.3
5179	0.328	0.312	-0.016	4.9	0.315	-.013	4.0
5180	0.047	0.047	0	0	0.047	0	0
Internally Sealed Concrete/							
5231	0.034	0.034	0	0	0.035	+.001	2.9
5232	0.006	0.006	0	0	0.006	0	0
5233	0.043	0.045	+0.002	4.7	0.045	+.002	4.7
5234	0.008	0.009	+0.001	12.5	0.008	0	0
Latex Concrete/							
5379	0.187	0.192	+.005	2.7	0.195	+.008	4.3
5380	0.038	0.036	-.002	5.3	0.036	-.002	5.3
5381	0.279	0.298	+.019	6.8	0.294	+.015	5.4
5382	0.118	0.116	-.002	1.7	0.119	+.001	0.8

Concrete Type/ Sample No.	% Cl^- Method I 1/	% Cl^- Method II 2/	Difference (II - I)	% Difference (II - I/I)	% Cl^- Method II 3/	Difference (II - I)	% Difference (II - I)
Latex Concrete/							
5283	0.321	0.315	-.006	1.9	0.319	-.002	0.6
5284	0.138	0.141	+.003	2.2	0.139	+.001	0.7
5285	0.343	0.337	-.006	1.7	0.357	+.014	4.1
5286	0.152	0.139	-.013	8.6	0.153	+.001	0.7
Average Values (lbs/yd = % Cl X 39.15)			0.0043	2.9%	-	0.0032	2.1%

$lb/yd^3 = 0.592\ kg/m^3$

1/ Method I: Potentionmetric titration using Cl^- electrode
2/ Method II: Gran plot procedure using Cl^- electrode
3/ Same as 2., but using Ag+ electrode

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