CHLORIDE ANALYSIS OF CONCRETE BY ION-SPECIFIC POTENTIOMETRY — ITS IMPLEMENTATION IN VIRGINIA

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SUMMARY

In response to an urgent request from the Materials Division, a literature search was conducted to find a suitable analytical method for the determination of chloride in hardened concrete. It was found that an ion-specific potentiometric method employing a chloride-extraction procedure improved by H. A. Berman of the Federal Highway Administration was the best available. Subsequent laboratory evaluation of this method indicated it to be good as far as accuracy and precision are concerned; however, modifications were needed, specifically on the titration procedure, to reduce analysis time and to eliminate analytical uncertainty involved when samples have extremely low chloride contents. Consequently, important modifications were made and a final analytical procedure is recommended for implementation by the Department.

1434

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INTRODUCTION

Problems resulting from the use of deicers such as sodium chloride and calcium chloride, which stimulate deterioration of concrete as well as corrosion of its steel reinforcement, are of major concern in highway maintenance. In order to better evaluate the extent of damages done by such deicers when deck repairs are made, chloride analysis of concrete samples is used to supplement the results from the electrical half-cell corrosion detection technique.

The chemical analysis of chloride in concrete used to be difficult and time-consuming and, because of the complexity of the procedure involved, was very inaccurate. The recent development of ion-specific potentiometric electrodes, which revolutionized the entire field of chemical potentiometry, has provided, among other uses, a simplified and relatively accurate technique for chloride analysis.

Since ion-specific potentiometry has been in existence for only a short time, the Virginia Department of Highways and Transportation did not possess the expertise and the specialized equipment needed to perform chloride analysis using the technique. This was brought to the attention of the Research Council by requests from the Department's Materials Division for chloride analysis of concrete samples from several bridge decks. Also, it has been indicated that chloride analysis of bridge decks in the state will be needed on a routine basis, so that it will be extremely useful for Materials Division personnel to learn the technique.

In response to this need, a literature search was conducted.[1,2,3] It was found then that an ion-specific potentiometric method employing a chloride extraction procedure improved by H. A. Berman of the Federal Highway Administration was the best available. Therefore, a project was initiated to evaluate the analytical reliability of the method. Furthermore, the procedure as outlined in Berman's method was carefully examined and,

as a result, some minor modifications were made that improved the overall performance of the method. Finally, the modified method was presented to the Materials Division, through an informal instructional and discussion session, for implementation in Virginia.

This report describes the brief study conducted and the modifications made to the method for chloride analysis. The modified procedure is also described and outlined.

APPARATUS AND CHEMICAL REAGENTS

Apparatus

1. A solid state chloride-ion specific electrode (Model 94-17) and a double junction reference electrode (Model 90-02), both manufactured by Orion Research, Inc.

2. An Accumet 520 pH/ion meter manufactured by Fisher Scientific Company.

3. Strip chart recorder.

4. Magnetic stirrer and teflon stirring bars.

5. Burette with 0.1-ml graduations.

6. Automatic syringe (50-ml capacity), manufactured by Sage Instruments.

Chemical Reagents

1. Concentrated nitric acid (HNO_3).

2. Sodium chloride (NaCl), reagent grade, for use as a primary standard.

3. Standard 0.01N NaCl solution. Dry reagent grade NaCl in an oven at $105^{\circ}C$. Cool, weigh out 0.5844g, dissolve in distilled H_2O, and transfer to a 1-liter volumetric flask. Make up to the mark with distilled H_2O and mix.

4. Standard 0.01 N $AgNO_3$ solution. Weigh 1.7g of reagent grade $AgNO_3$, dissolve in distilled H_2O, filter into a 1-liter brown glass bottle, fill, and mix thoroughly. Standardize by titration with 20ml of the 0.01N NaCl solution.

EVALUATION OF THE METHOD

The method is fairly simple. Basically, a powdered concrete sample is digested with an HNO_3 solution to extract the chloride. The chloride is then titrated with an $AgNO_3$ solution, which is represented by

$$Cl^- + AgNO_3 \longrightarrow NO_3^- + AgCl_{(s)}$$

As this reaction proceeds, the electrical potential between the chloride-ion specific electrode and the reference electrode changes. By measuring this potential as the chloride is being titrated with $AgNO_3$, the endpoint of the reaction is determined. Figure 1 shows a typical curve of potential readings versus volume of $AgNO_3$ solution added, where the endpoint is the point of inflection of the curve. Knowing the volume (V) of the standard $AgNO_3$ solution required to titrate the sample, as indicated by the endpoint, one can calculate the concentration of chloride in the sample. Figure 2 shows the titration setup.

The reproducibility of the method was tested by multiplicate analyses of several prepared samples with different chloride concentrations. Table 1 shows the mean standard deviation that could be expected of an individual analysis to be 0.004% chloride, which is a measure of the combined precision of the method, consisting of extraction and titration of the chloride. This precision is relatively good for the chloride concentrations involved.

The accuracy of the method is more difficult to estimate than its reproducibility because there is no suitable independent analytical technique against which the method could be tested. Nevertheless, several powdered concrete samples (some of these were kindly supplied by H. A. Berman of the Federal Highway Administration) of known chloride concentrations were analyzed to estimate the accuracy of the method. Table 2 shows that, except for sample 3, the agreement between the known and the determined concentrations is good, with the mean absolute difference being -0.002. The large discrepancy for sample 3 must be attributed to errors caused by the migration or loss of chloride during making of the standard specimen.
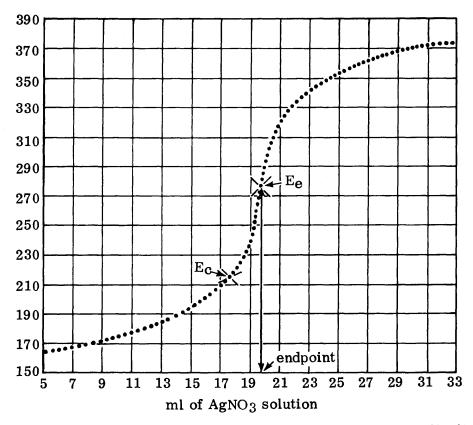
Figure 1. A potentiometric titration curve plotted as millivolt versus volume of AgNO$_3$ solution added.

Figure 2. The titration setup.

Table 1

Comparison of Multiplicate Chloride Analyses on Ground Concrete Samples.

Sample	Chloride Concentration (%)	Standard Deviation, S, (%)
1	0.011	
	0.013	
	0.013	0.001
2	0.031	
	0.033	
	0.033	
	0.033	
	0.033	0.001
3	0.062	
	0.049	
	0.065	
	0.059	0.008
4	0.304	
	0.303	
	0.302	
	0.305	
	0.304	0.002

Mean Standard Deviation $= \dfrac{\sum S}{4} = 0.003\%$

Table 2

Chloride Concentration of Standard Specimens.

Sample	Chloride Concentration (%)		
	Known	Determined	Absolute Difference, d,
1	0.596	0.601	+ 0.005
		0.592	− 0.004
2	0.316	0.318	+ 0.002
		0.319	+ 0.003
3	0.043	0.033	− 0.010
		0.033	− 0.010
4	0.019	0.019	0
		0.019	0

Mean Absolute Difference $= \dfrac{\Sigma d}{8} = -0.002\%$

MODIFICATION OF PROCEDURE

The accuracy of the titration procedure depends on how well the endpoint can be estimated. From experience, it has been found that it is best to plot the curve (Figure 1) of millivolt readings versus volume of $AgNO_3$ solution added for each analysis to estimate the endpoint. However, it takes about fifteen minutes to take the millivolt and the volume of titrant readings and to plot them into a curve. When numerous samples are involved, as always is the case, these fifteen minutes add up to a significant amount of testing time. For this reason, the authors felt that a simple automatic titration system would be helpful in reducing the analytical time. In order for such an automatic titration to be feasible, the difficulty which arose from the need for the standard $AgNO_3$ solution to be delivered at a constant rate, which is not possible with a conventional gravity-flow burette, had to be overcome. This was done by using a moter driven hypodermic syringe with a predetermined flow rate in place of the conventional burette. (If a motor driven syringe is not available, a constant head reservoir, e.g., mariottle bottle, can be used.) With the $AgNO_3$ solution being added to the sample solution at a constant rate (5ml/min is most desirable) by a motor driven hypodermic syringe, the automatic titration system

is completed simply by connecting a strip chart recorder to the pH/ion meter. This system (Figure 3) worked perfectly and eliminated most, if not all, of the time needed before to take the millivolt and the volume of $AgNO_3$ readings and the manual plotting of the titration curve. This saving in time is at least equivalent to one dollar per sample.
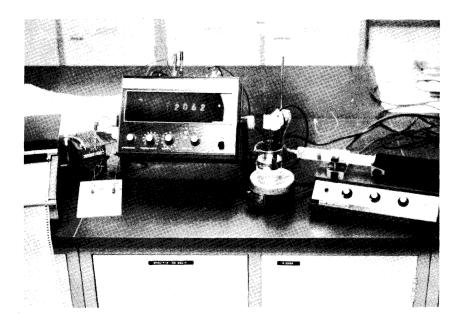

Figure 3. A titration setup automated by the use of a motordriven hypodermic syringe and a strip chart recorder.

The other aspect of the procedure that the authors felt could be improved pertained to the titration of samples with extremely low chloride contents ($\leq$ 0.02%). In a personal communication regarding some ground concrete samples that he kindly provided, Mr. Berman suggested that for samples with low chloride contents, the endpoint is extremely difficult to estimate with good accuracy unless the sample solution is spiked with a known volume of the standard NaCl solution. However, this raised the question of how one could know, before analyzing a sample, that the sample has a low chloride content and will pose a problem. In other words, an indicator is needed to let the analyst know before proceeding with the titration of a low chloride sample that he needs to spike it first with an NaCl solution. In Figure 1, one can see that the critical region in a titration is from E_c to E_e, where E_e is the voltage corresponding to the endpoint. This region, corresponding to a voltage difference of about 60 mV, is critical because it is characterized by a high voltage change per unit change in volume of titrant added. When one is titrating a sample of extremely low chloride content, the initial voltage reading

may be well within the critical region such that it is difficult, or nearly impossible, to estimate the inflection point of the curve, or endpoint, accurately.
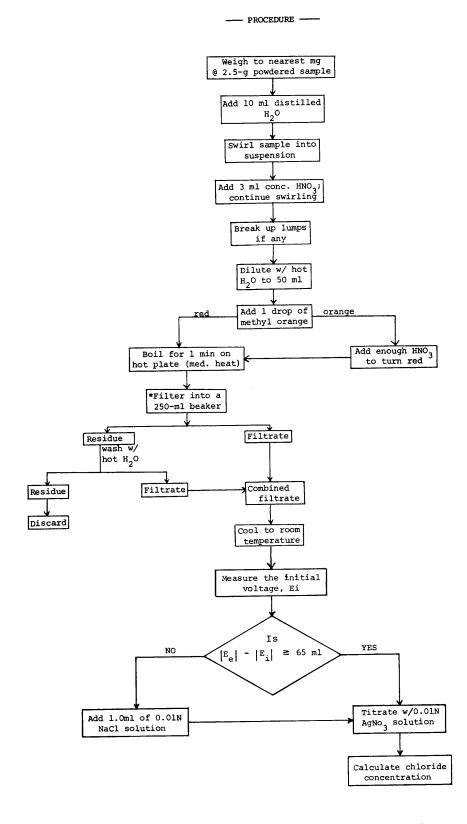
From experience, it has been found that for a given system of electrodes and ion meter, the voltage reading corresponding to the endpoint is practically constant; for the Council system this is approximately 275 mV. This constancy of the endpoint voltage reading provides a satisfactory indicator by which an analyst can judge before titration whether he should spike the sample solution with an NaCl solution. He simply takes note of the initial voltage reading and if this is within 60 mV of the endpoint voltage for his system, he should spike his sample solution with a known amount of 0.01N NaCl solution then proceed with the titration. After the titration, he should subtract from the total volume of 0.01N $AgNO_3$ solution needed to reach the endpoint the volume of the $AgNO_3$ solution equivalent to the added NaCl solution. This approach has been found to be very satisfactory.

CONCLUSION AND RECOMMENDATION

This study has found that the improved Berman ion-specific potentiometric method for the determination of chloride in concrete is basically good as far as precision and accuracy are concerned. However, it needed modifications to reduce the analysis time and to eliminate the difficulty encountered when dealing with samples of low chloride content. Such modifications were made and the final procedure, outlined below, is thereby recommended for use by the Department.

METHOD OF TEST FOR CHLORIDE IN CONCRETE

1. Scope

    1.1 This method covers a procedure for the determination of the chloride content of concrete.

2. Apparatus

    2.1 Chloride-ion selective electrode and manufacturer-recommended accessory solutions.

    2.2 A millivometer or pH-meter compatible with the ion electrode.

    2.3 Magnetic stirrer and teflon stirring bars.

3. Reagents

    3.1 Concentrated HNO_3

    3.2 NaCl, reagent grade (primary standard)

    3.3 Standard 0.01N NaCl solution. Dry reagent grade NaCl in an oven at $105^{\circ}C$. Cool, weigh out 0.5844 g, dissolve in distilled H_2O, and and transfer to a 1-liter volumetric flask. Make up to the mark with distilled H_2O and mix thoroughly.

    3.4 Standard 0.01 N $AgNO_3$ solution. Weigh 1.7 g of reagent grade $AgNO_3$, dissolve in distilled H_2O, filter into a 1-liter brown glass bottle, fill, and mix thoroughly. Standardize by titration with 20 ml of the NaCl solution.

4. Procedure (see flow chart)

—— PROCEDURE ——

```
        ┌─────────────────────────┐
        │  Weigh to nearest mg    │
        │ @ 2.5-g powdered sample │
        └────────────┬────────────┘
                     │
        ┌────────────┴────────────┐
        │  Add 10 ml distilled    │
        │          H₂O            │
        └────────────┬────────────┘
                     │
        ┌────────────┴────────────┐
        │   Swirl sample into     │
        │      suspension         │
        └────────────┬────────────┘
                     │
        ┌────────────┴────────────┐
        │ Add 3 ml conc. HNO₃;    │
        │   continue swirling     │
        └────────────┬────────────┘
                     │
        ┌────────────┴────────────┐
        │   Break up lumps        │
        │       if any            │
        └────────────┬────────────┘
                     │
        ┌────────────┴────────────┐
        │   Dilute w/ hot         │
        │   H₂O to 50 ml          │
        └────────────┬────────────┘
                     │
  red   ┌────────────┴────────────┐  orange
  ◄─────│   Add 1 drop of         │─────►
        │   methyl orange         │
        └─────────────────────────┘
```

Add 1 drop of methyl orange — H_2O to 50 ml

Add enough HNO_3 to turn red

Boil for 1 min on hot plate (med. heat)

*Filter into a 250-ml beaker

Residue wash w/ hot H_2O

Filtrate

Residue

Discard

Filtrate

Combined filtrate

Cool to room temperature

Measure the initial voltage, Ei

Is $|E_e| - |E_i| \geq 65$ ml

NO

YES

Add 1.0ml of 0.01N NaCl solution

Titrate w/0.01N $AgNo_3$ solution

Calculate chloride concentration

*NOTE Use a double thickness of filter paper, consisting of a medium-porosity paper under one of high porosity.

CALCULATION

Case 1: No NaCl solution added before titration.

$$P = \frac{3.5453\, N_a V_a}{W}$$

where P = percent chloride by weight in concrete

W = weight of ground concrete sample in grams

N_a = normality of the $AgNO_3$ solution

V_a = volume of $AgNO_3$ solution, in ml., added up to the endpoint

*NOTE: Use an automatic syringe (or equivalent) in conjunction with a strip chart recorder.

Case 2: NaCl solution added before titration.

$$P = \frac{3.5453\, N_a}{W} \left(V_a - \frac{N_n V_n}{N_a} \right)$$

where N_n = normality of the NaCl solution, in ml., added before titration with $AgNO_3$ solution

V_n = Volume of NaCl solution, in ml., added before titration with $AgNO_3$ solution

while P, W, N_a, and V_a are the same as in Case 1.

1446

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1448