

DETERMINATION OF CHLORIDE ION CONTENT IN CONCRETE
3-C-3-113

By

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SUBJECT

Analysis of hardened concrete for chloride ion content.

PURPOSE

This project was undertaken to improve laboratory testing procedures for chloride ion content in concrete in terms of time and work required and quality of results obtained.

BACKGROUND

The determination of chloride ion content in concrete has been performed as a standard procedure by the Texas State Department of Highways and Public Transportation for a number of years. Water-soluble chlorides from deicing salt or natural sources have been found to penetrate concrete over extended time periods. In high enough concentrations, chlorides are believed to accelerate corrosion of reinforcing steel or weaken the concrete. In order to detect potential problems, four-inch diameter cores are taken from bridge decks or other sources prior to major maintenance work and analyzed for chloride content in one-inch layers starting at the surface. Because the chloride source is external, the highest concentration is generally found at the surface.

Chlorides are found in concrete in the form of water-soluble salt anions and chemically tied-up chlorides in the cement. Methods are available for extracting the water-soluble chlorides and the total chlorides, the latter by means of acid digestion. According to the Federal Highway Administration, water-soluble chloride levels above 500 ppm in concrete are detrimental. The additional chlorides, which are acid soluble, are thought to not be as detrimental because they are not in a readily reactive form and will not accelerate steel corrosion.

As a result of the reasons mentioned above, chloride analysis by the Texas SDHPT has been done for water-soluble chlorides only. The procedure used prior to this work is explained in the Test Methods and Data section of this report.

CONCLUSIONS AND RECOMMENDATIONS

Hot water digestion of chlorides using a hot plate was found to be the most desirable method of sample preparation due to the minimal operator time and equipment required. The standard calibration method using an ionalyzer and specific ion electrodes is the preferred method of solution analysis. Two calibration methods are suitable for use: titration of a sample solution and use of a known concentration calibration solution. Use of a titration provides greater accuracy, particularly if the titrant normality is sufficiently low to give a distinct endpoint. Accuracy within five percent is possible only if at least two mls of titrant is used. There are no significant interfering substances apparent in the titration of the sample solutions.

The recommendations resulting from this work are to use the hot water digestion and standard calibration methods referred to above. The recommended method for determining chloride ion content is outlined in detail in the appendix.

MATERIALS AND EQUIPMENT

All analyses were performed using actual concrete core samples received for routine analysis. Approximately 180 cores representing 20 bridge locations were used to gather the data shown in this report. The methods adopted have been monitored during analysis of several hundred samples.

Chloride ion was titrated with silver ion in the form of silver nitrate. The solutions required for this titration were silver nitrate, 0.01 N or 0.1 N, methyl red indicator, and dilute nitric acid. The silver nitrate

solutions were prepared from A.C.S. reagent grade silver nitrate and standardized by titration with a primary standard solution prepared from A.C.S. reagent grade sodium chloride. The methyl red indicator solution was prepared by dissolving 0.1 gram methyl red A.C.S. analytical reagent in 50 ml of 60 percent by volume ethanol. Nitric acid solution was prepared by mixing one part by volume A.C.S. grade concentrated nitric acid to ten parts by volume deionized water.

The acid digestion method used A.C.S. grade concentrated nitric acid and methyl orange solution prepared by dissolving 0.1 gram methyl orange indicator in 100 ml deionized water.

Sample solutions prepared by the water digestion and acid digestion methods were analyzed using an Orion Model 801 A ion meter fitted with a chloride selective-ion electrode (Orion Model 94-17B) and a double-junction reference electrode (Orion Model 90-02). Reference electrode filling solutions were those specified by the manufacturer, the outer solution being ten percent potassium nitrate.

Analyses by atomic absorption were accomplished using a Perkin-Elmer Model 3030 Atomic Absorption Spectrophotometer equipped with Perkin-Elmer hollow-cathode lamps. Solutions for atomic absorption analysis are detailed in the section titled Test Methods and Data.

The reflux extraction method of sample preparation used a Soxhlet extraction tube with a Friedrichs condenser and boiling flask. Extraction thimbles made of fritted glass and of paper were used.

TEST METHODS AND DATA

The method of sample preparation and analysis used prior to this research determined the water-soluble chloride ion content by titration with silver nitrate. In this method, a 30-gram sample of concrete core ground to pass

a Number 60 sieve is transferred into a 400 ml beaker with 300 ml of deionized water. The beaker with sample is heated to 150 ± 20 F for a minimum of eight hours, the solution decanted, core material filtered and washed, and liquid sample volume made up to 500 ml. A 50 ml sample of this solution is pipetted into a beaker, acidified to a pink methyl red endpoint, and potentiometrically titrated with silver nitrate by use of a chloride selective-ion electrode.

Certain characteristics of the water digestion and titration were observed during the project. Repeated titration of a sample showed excellent consistency, as would be expected.

Table 1 shows this repeatability when using 0.01 N silver nitrate. A more concentrated silver nitrate solution will not give such high quality repeatability or accuracy.

Repeating the digestion and analysis processes for a particular sample showed the repeatability of the digestion method. Table 2 has data to illustrate this.

An initial attempt was made at determining a direct correlation between chloride concentration and the initial millivolt (IMV) reading given by the chloride selective-ion electrode and ion meter. This solution conductance reading (IMV) is taken before addition of titrant. There are factors which may affect the accuracy of the titration and the IMV reading, including interfering or competing ions, pH, temperature, ionic strength, and electrode condition. Although a strong correlation between chloride concentration and initial millivolt reading existed over a large range of concentration, it was evident that certain variations were occurring within a small concentration range. There was also instability with time. A comparison of core sample solutions with prepared sodium chloride solutions indicated little competing ion effects in the titration and relatively little interference with the millivolt readings. This was

checked by comparing titration results for samples whose IMV readings were the same, within a tolerance of one millivolt. A difference in the value determined by titration would indicate the presence of other ions consuming the silver nitrate. The presence of competing ions could cause the titration to give less accurate results than methods based on millivolt readings of the chloride probe. Since competing ion effects appear to be small, the titration has been accepted as the reference method for this work. The temperature compensation ability of the meter apparently negated any adverse solution temperature effects. It became obvious that fluctuations in the reference electrode solution levels and changes in the selective-ion electrode sensitivity with time would lead to variations in the IMV reading. The pH, by controlling solution ionic strength, also affected the IMV reading.

In order to obtain control over the factors mentioned, the methods of standard calibration, known addition, known subtraction, analate addition, and analate subtraction were considered. These methods except for standard calibration, are incremental methods which involve addition of either standard or sample solution in a known volume to the other solution. The analate solution is the sample solution. Standard calibration and known addition were studied. The known addition method involved measuring the IMV of a known volume (100 ml) of sample, adding a known volume (10 ml) of a known concentrated standard solution, and remeasuring the IMV. The sample concentration is determined from the following equation:

$$[\text{Sample}] = \frac{P[\text{Standard}]}{\pm (1-(1+P) 10 \Delta \text{IMV}/S)} \quad \text{where } P = \frac{\text{Std. Vol.}}{\text{Sample Vol.}} \quad S = \text{electrode slope}$$

Results from this method may be found in Table 3.

Analysis by standard calibration was used for a large number of samples. Samples were prepared by hot water digestion using 30 grams of core. In the standard calibration method, approximately 50 ml of sample is acidified to a pink methyl red end point using nitric acid and an IMV reading is taken

without titration. The readings for the unknowns are then compared to the IMV reading for a known concentration prepared standard or a titrated unknown. A detailed description may be found in the procedure in the appendix. Table 4 gives a comparison of results obtained by titration versus those obtained by standard calibration using prepared standards.

Analysis by standard calibration using a titrated sample as a calibration standard was performed on several sets of cores. The solution used as a standard was chosen at random from each set. The advantage of using this type of standard is that the unknowns and the standard are from the same location and have very similar compositions. Table 5 shows results of one set of cores analyzed using this method.

Atomic absorption analysis was used for chloride analysis on samples prepared by hot-water digestion. The quantitative determination was based on silver analysis because the element chlorine does not respond to atomic absorption techniques. The solutions used in this method follows:

Silver Standard Stock: 500 ppm silver ion, 5 percent by volume nitric acid. Prepared from 0.7873 grams silver nitrate and 83.3 ml concentrated nitric acid diluted to 1000 ml.

Blank: 0 ppm silver ion, 10 ppm sodium ion, 5 percent by volume nitric acid. Prepared from 10 ml sodium stock, 41.7 ml concentrated nitric acid diluted to 500 ml.

Silver Standard 1: 10 ppm silver ion, 10 ppm sodium ion, 5 percent by volume nitric acid. Prepared from 10 ml silver standard stock, 10 ml sodium stock, and 41.7 ml concentrated nitric acid diluted to 500 ml.

Silver Standard 2: 20 ppm silver ion, 10 ppm sodium ion, 5 percent by volume nitric acid. Prepared from 20 ml silver standard stock, 10 ml sodium stock, and 41.7 ml concentrated nitric acid diluted to 500 ml.

Silver Check 1: 5 ppm silver ion, 10 ppm sodium ion, 5 percent by volume nitric acid. Prepared from 5 ml silver standard stock, 10 ml sodium stock, and 41.7 ml concentrated nitric acid diluted to 500 ml.

Silver Check 2: 15 ppm silver ion, 10 ppm sodium ion, 5 percent by volume nitric acid. Prepared from 15 ml silver standard stock, 10 ml sodium stock, and 41.7 ml concentrated nitric acid diluted to 500 ml.

Silver Reagent Stock: 9132 ppm silver ion, 5 percent by volume nitric acid. Prepared from 3.596 grams dried silver nitrate, 20.8 ml concentrated nitric acid diluted to 250 ml.

Silver Reagent: 182.7 ppm silver ion, 5 percent by volume nitric acid. Prepared from 10 ml silver reagent stock and 41.7 ml concentrated nitric acid diluted to 500 ml.

Sodium Stock: 667. ppm sodium ion. Prepared from 1.23 grams sodium nitrate dissolved in 500 ml.

Sodium Sample Solution: 66.7 ppm sodium ion, 33 percent by volume nitric acid. Prepared from 50 ml sodium stock and 278 ml concentrated nitric acid diluted to 500 ml.

The atomic absorption sample preparation used chloride samples prepared by hot-water digestion of salts from 30 grams of core sample and made up to a volume of 500 ml. The sample preparation and analysis follow. Quantitatively, 10 ml each of the chloride sample and the silver reagent solution are mixed together and allowed to react for one hour. This mixture is filtered, using highly retentive paper and vacuum filtration apparatus, the solids washed, and the filtrate and washings collected in a 100 ml volumetric flask. After addition of 15 ml of sodium sample solution, the sample is diluted to 100 ml. This sample contains 5 percent by volume

nitric acid, which keeps silver nitrate in solution, 10 ppm sodium ion, which is an ionization suppressor during flame atomization in the atomic absorption process, and either silver or chloride ion. Some samples were also prepared by doubling the amount of each reagent, resulting in a sample solution volume of 200 ml. Data for these analyses are included in Table 4. The sample preparation step which mixes silver nitrate with sodium chloride results in the formation of silver chloride precipitate. This reaction, particularly in acidic conditions, goes essentially to completion, leaving only silver or chloride ions in solution. The amount of silver nitrate provided is sufficient to consume exactly 1000 ppm chloride, based on the 30 gram core sample. Any chloride level under 1000 ppm will result in excess silver ion, the concentration of which, detected by atomic absorption, indirectly gives the sample chloride level. If no silver is detectable during analysis, the sample chloride level was at least 1000 ppm, but the exact concentration is unknown.

Atomic absorption analysis for silver is done using a lean, blue air-acetylene flame, a wavelength of 338.3 nm, and a slit width of 0.7 nm. After making flame and nebulizer adjustments using a copper standard, the instrument silver signal is zeroed using the blank solution. Silver standards S1 and S2 are used to calibrate the instrument and check solutions C1 and C2 are used to check the stability of the operation. The maximum silver level detectable, 18.3 ppm, corresponds to no chloride. The chloride level is calculated as follows:

$$\text{ppm Chloride} = 1000 - 54.73 (\text{ppm Silver})$$

Table 6 shows results of atomic absorption analysis using both preparation methods.

Two additional methods of sample preparation were studied: acid digestion and water reflux. These methods were considered as potential replacements for the hot-water digestion method. Neither would require a specific method of analysis.

The acid digestion method used was the procedure for total chloride content as outlined in the Federal Highway Administration's report Number FHWA-RD-77-85. This method differs from other techniques in that total chloride content, which exceeds the water soluble content, is determined. In this method a three gram sample of well-ground core is transferred into a mortar. After adding 10 ml of hot water, a pestle is used to grind the sample to a specified fineness. The sample is transferred to a 100 ml beaker. The mortar is rinsed first with three ml concentrated nitric acid and then with deionized water into the 100 ml beaker. The solution is made up to 50 ml with hot water, methyl orange is added, and nitric acid is added until a pink or red end point is reached. The beaker is covered with a watch glass, placed on a hot plate, and the solution is gently boiled for one minute. The sample solution is filtered into a 250 ml volumetric flask and diluted to volume. Analysis was then done by silver nitrate titration. Results are in Table 7.

The water reflux method of sample preparation involved use of a Soxhlet extraction unit with attached condenser and boiling flask. Extraction thimbles made of fritted glass and paper were used as sample containers within the Soxhlet unit. The Soxhlet unit works by boiling water in the flask, condensing the vapors in the condenser, and catching the hot condensate in the Soxhlet extraction tube. The hot condensate collects in and around the sample-containing thimbles. Upon attaining a specified liquid level, a siphon tube draws off the hot liquid which contains salts leached from the core material. This process, which required 20 to 30 minutes per cycle, was repeated for a total of 6 to 7 hours. The resulting salt-laden solution was then made up to a specified volume and analyzed for chloride content using the standard methods described herein. This method was intended to combine the digestion and filtration steps into one process, but the resulting solutions had to be filtered due to carry-over of fines. Attempts to prevent this were unsuccessful. The extraction process was done using both 15 and 30 gram samples. Typical results are shown in Table 8 for a single core sample. The hot-water digestion method yielded a chloride content of 320 ppm on the same sample.

RESULTS AND DISCUSSION

The silver nitrate titration was considered for this work as a reference method with which other methods could be compared. It is a standard method of analysis and is the method of choice of ASTM for analysis of cement. This work showed that the titration is very repeatable for any particular sample. The possibility of interfering or competing ions in the titration was considered. Notable interferences in this titration are bromide, iodide, and sulfide ions. Potential interferences in the operation of the ion-selective electrode are bromide, hydroxide above pH 11, fluoride, sulfide, iodide, and cyanide. Nitrate, sulfate, and bicarbonate do not interfere with the electrode. It is believed that none of the above interferences occur in typical concrete samples to a noticeable extent. This was verified by comparison of millivolt readings for different samples whose chloride concentration by titration was the same or very nearly so. Also, the electrode response slope was determined using actual core samples and prepared sodium chloride solutions. The response slope is the change in millivolt reading per tenfold change in concentration. There was no difference in the response slopes determined by these two methods. A difference would be expected if those cores high in chlorides were also high in other titratable salts.

Variations in the initial millivolt (IMV) reading can be tied primarily to solution ionic strength and matrix effects, reference electrode filling solutions, and instrument calibration. Instrument calibration may drift over long time periods, but this does not appear to create any problems for a single day's analysis work. The levels and concentrations of the filling solutions are also variables which are easily controlled and do not effect short-term stability. Solution ionic strength can greatly affect the IMV reading and use of an ionic strength adjustor (ISA) or pH adjustor is necessary to obtain good stability. The ISA recommended by Orion for the chloride electrodes is 5 M sodium nitrate solution. This ISA did not provide as good stability or repeatability as the pH adjustor normally used for the silver nitrate titration. This pH adjustment is to a

pink methyl red endpoint using nitric acid. The core sample solution matrix is in almost all cases slightly basic as a result of other salts leached from the core material. The effect of solution temperature on the IMV reading is negligible for commonly encountered solution temperatures.

The hot-water digestion method, as shown in Table 2, gives very good accuracy and repeatability as long as adequate temperatures are maintained and thorough washing is performed. Use of cold water may result in incomplete washing of the fines. This method requires that each sample be filtered and washed, requiring an investment of perhaps one hour operator time for a group of 12-15 samples. In order to thoroughly dissolve the salts, the sample in its beaker must be kept on a hot plate for a period of several hours. This is typically done overnight. The entire analysis process, from weighing the dry core material to analyzing for chloride content in solution, normally requires two days using this method.

The two alternate sample preparation methods were studied with the intent of reducing the work load required and speeding the analysis process. The acid digestion method, in addition to having poorer repeatability, is a very labor intensive process in comparison to the water digestion method. The complete analysis of a single sample may be done in one hour, but analysis of a group of 12-15 samples could require one worker the majority or all of an eight-hour day. The repeatability of the method based on titration was poor and the control on solution pH was also poor. This led to poor reproducibility of the IMV reading and instability in this reading.

The reflux method of sample preparation showed promise in that the time-consuming filtration step could be eliminated. In practice, however, this did not occur due to carry-over of fines. The quantity carried over was small enough that the analysis could probably have been done without filtration without affecting accuracy or severely shortening the probe life. The paper thimbles were preferable to the glass thimbles in that the condensate flowed more readily through the paper thimble while the Soxhlet unit was

siphoning. This leads to the conclusion that the paper thimbles are more efficient although the results showed no real difference after the six-hour period. The reflux method required nearly the same amount of operator work as the water digestion method because of the equipment set-up, monitoring, and dismantling. The method worked best with the smaller 15-gram sample and appeared to give very thorough washing of the salts.

The known addition analysis method gave results which varied widely from those obtained by titration. For example, a sample with 460 ppm chloride by titration gave chloride concentrations of 775 and 815 ppm by known addition. Consistent results could not be obtained. This method is fairly simple, but does not appear to be suitable for this analysis.

The standard calibration method makes use of a known concentration standard solution, which calibrates the electrodes, and the known response slope of the electrodes. The solution chosen as the standard and the method of determining its concentration will control the accuracy of the method. The factors previously mentioned which affect the IMV must be considered in selecting the standard. The data collected and displayed in Table 4 are based on a standard solution prepared from sodium chloride as outlined in the appendix. The standard pH is more acidic than the sample pH because of the other dissolved salts in the sample. Treatment with acid alleviates the pH difference, but the possibility exists that the salts present might contain interferences which lower accuracy. The acid treatment does provide equivalent ionic strength between standard and samples. Other types of standard solutions with more similar composition may be used or a single titration may be performed and referenced as a standard. Results of the standard calibration method using a titration are shown in Table 5. This method gives better accuracy than using a prepared standard, particularly for higher chloride concentrations where the titration is more accurate. For chloride concentrations below about 150 ppm, based on the concrete, the standard solution appears to provide equal or superior accuracy. The titration accuracy varies with the solution normality and volume of titrant used.

The standard calibration procedure is advantageous in that there is less operator work required and the procedure is much less time consuming than the silver nitrate titration. Use of silver nitrate is greatly reduced and electrode life should be prolonged because there is little or no silver chloride precipitating onto the electrode surfaces.

All of the sample solutions used to gather data for the standard calibration methods were actually titrated. Based on a comparison of the titrated results to the "predicted" results by standard calibration, the average deviation for the standard calibration method results shown in Table 4 using a 500 ppm standard is 11 percent and the standard deviation is 15 percent. The average concentration for the solutions shown in Table 4 is 375 ppm with an average deviation of 34 ppm from the titrated value. The average deviation for the analyses run using a titrated sample as a standard was seven percent and the standard deviation of the error was 11 percent. The average concentration and deviation for this method was 492 ± 30 ppm. The sample solutions chosen to be the titrated standard were necessarily chosen somewhat at random, one from each set analyzed, although generally one of the higher concentration (low IMV) solutions was chosen. By plotting the titration results against the standard calibration results, a correlation coefficient was determined. This is an indication of the ability of the methods to correlate the IMV reading to the chloride content. The correlation for the data in Table 4 is 0.990. The correlation for the analyses using a titrated standard averaged 0.993 and ranged from 0.984 to 0.999. The correlation coefficients show no significant difference between the methods, but the percentage deviation and standard deviation data show the titrated standard method to be slightly superior. It is recognized that the deviation between the titration results and standard calibration results is not necessarily an indication of error in the standard calibration method. The titration is susceptible to errors from dissolved salts that will not affect the specific ion electrode. However, this work has indicated that the titration is very reliable and deviations from it by other methods are probably errors.

The atomic absorption method is somewhat more labor-intensive than the other methods due to the extra sample preparation required. The analysis itself is, however, very rapid. Instrument preparation requires approximately fifteen minutes and analysis requires only about fifteen seconds per sample. The short analysis time makes this method more attractive for analysis of large numbers of samples at a time. The method does require use of more glassware and reagents and as a result there is more cleanup involved.

Reproducibility of the analysis and preparation methods is very good. In almost all cases, the chloride concentration by AA was high if it was in error. This corresponds to a low silver content which may have been caused by adsorption of silver ions onto the precipitate. The AA instrument sometimes has fluctuations in sensitivity, generally due to problems with the sample delivery system. Collection of solids within the nebulizer may occur, reducing the sample uptake rate and therefore the apparent concentration. This method has the advantage that fluctuations in sensitivity can be easily detected during the course of analysis by the use of standard solutions. If fluctuations are observed, the instrument can be cleaned to restore optimum performance and the erroneous samples can be reanalyzed. Results obtained from preparation of 200 ml of sample instead of 100 ml showed definite improvement, although the amount of data obtained is limited. After a technique was developed, the method did correlate well with the titration and further refinement of the method is possible. Atomic absorption has the advantage over the silver nitrate titration and standard calibration methods that there are likely to be fewer chemical interferences because the AA instrument is very element specific. Other types of interferences which may occur in AA analysis were eliminated by the method of sample preparation, as discussed in the Test Methods section.

APPENDIX

TEST METHOD FOR DETERMINATION OF CHLORIDE IN CONCRETE

DETERMINATION OF CHLORIDE IN CONCRETE

Scope

This test procedure is intended for use in determining the percent by weight of water soluble chloride in concrete. This method uses a direct reading chloride analysis with a standardizing solution which is based on silver nitrate titration as a reference. The silver nitrate titration is explained within this test procedure. Errors in the silver nitrate titration due to interfering substances in concrete are assumed to be negligible.

It should be noted that the calibration curves and equations in this procedure are instrument-specific and may not be applicable to different equipment. Individuals wishing to use this method with different equipment must prepare their own calibration curve as described within this procedure.

Apparatus

1. Diamond-tooth saw or other means of segmenting concrete cores and producing a smoothly-cut surface.
2. Jaw crusher which is capable of reducing material so as to pass a No. 10 sieve.
3. Mechanical pulverizer which is capable of reducing material so as to pass a No. 60 sieve.
4. No. 60 U. S. Standard sieve in compliance with Test Method Tex-907-K.
5. Mechanical convection oven with temperature maintained at 140 ± 20 F.

6. Balance with a minimum capacity of 100 grams which meets the requirements of Test Method Tex-901-K, Class 1-B.
7. Electric hot plate.
8. Beaker, Griffin Low Form, 400 ml capacity with watch glass and stirring rod.
9. Beaker, Electrolytic High Form, 180 ml capacity.
10. Flask, Class A Volumetric, 500 ml capacity with stopper.
11. Gravity Filtration Funnel, ribbed.
12. Filter paper, No. 2 Micro Filtration Systems or equivalent.
13. Chloride Selective-ion Electrode (Orion Model 94-17B or equivalent).
14. Reference Electrode (Orion Model 90-02 double junction or equivalent).
15. Ion meter (Orion Model 801A or equivalent) readable to 0.1 millivolts.
16. Electrically powered magnetic stirring device.
17. Teflon-coated magnetic stirring bar.
18. Pipet, Class A Volumetric, 50 ml capacity.
19. Buret, Class A, 25 ml capacity.
20. Hand-held magnet for use in removing metallic particles from the pulverized samples.

Solutions

1. Deionized or distilled water.
2. Methyl Red Indicator Solution - prepared by dissolving 0.1 gram Methyl Red A.C.S. Analytical Reagent (neutral or sodium salt) in 50 ml of 60 percent by volume ethanol. The ethanol used may be denatured.
3. Nitric Acid Solution - prepared by adding one part by volume A.C.S. grade concentrated nitric acid to ten parts by volume deionized water.
4. 0.01 N Silver Nitrate Solution - prepared from A.C.S. reagent grade silver nitrate. Solution must be standardized by titration with a sodium chloride solution prepared from dried A.C.S. reagent grade sodium chloride. Normality should be determined to at least three significant digits.
5. Reference electrode outer filling solution (Orion 90-00-03 or equivalent), 10 percent KNO_3 .
6. Reference electrode inner filling solution (Orion 90-00-02 or equivalent).
7. "500 ppm" Chloride Calibration Solution - prepared from dried A.C.S. reagent grade sodium chloride. A 10,000 ppm stock solution may be prepared by dissolving 1.978 grams of sodium chloride in one liter of deionized water. Dilution of a 50 ml aliquot to 1000 ml with deionized water yields a 500 ppm solution. This 500 ppm concentration is based on a 30 gram core sample and is not the true concentration of chloride in water.

Procedure

1. Sample Preparation. Concrete samples are to be obtained in the form of four inch diameter cores by use of a coring bit. Any asphaltic overlay material is to be removed from the surface face of the core. This cleaned face is the reference plane for subsequent core segmenting. Guide markings should be made around the core's circumference at exactly one inch and two inches from the core surface. Adjustment may be made for cores which contain steel reinforcing bar segments. The cores are to be cut into segments with faces parallel to the core surface such that the saw blade cuts through the center of the guide markings. Water may be used for lubrication and cooling of the saw blade.

Towel dry each core segment and place in the 140 F oven to dry for at least twenty-four hours. The dried segments are then crushed in the jaw crusher and ground further in the pulverizer. The resulting powder is hand-shaken through the #60 sieve and the magnet used to remove metal filings from the material passing the #60 sieve. The passed material is the sample material and is stored in the 140 F oven until it is to be analyzed.

2. Chloride Leaching. Mix the sample well and weigh a representative 30.0 ± 0.01 gram portion of the material. Transfer this to a clean 400 ml beaker, add 300 ml deionized water and stir, cover with a watch glass, and place on the hot plate. Adjust the hot plate to obtain a water temperature of 150 ± 20 F. Take care that the sample does not boil and that no sample solution is lost. Maintain the volume at 300 ± 25 ml by adding deionized water and stir the solution periodically. The sample solution may be removed from the hot plate after eight hours digestion time.

Set up a funnel with filter paper in a volumetric flask for each sample solution. Rinse off the stirring rod and watch glass underside into the funnel using deionized water. Decant as much solution as possible through the filter. Transfer the sample material into the filter funnel and rinse the beaker out with hot deionized water. Transfer the washings into the filter funnel. Repeated washings of the sample material must be performed, allowing the hot rinse water to drain through between washings. After the washings are complete, rinse off the filter paper and funnel surfaces into the flask. Fill the flask to the volumetric mark with deionized water and let the solution cool to 77 ± 2 F.

3. Chloride Analysis. Invert and shake the flask well to insure thorough mixing of the solution. Transfer 50 ± 10 milliliters of solution to a clean, dry electrolytic tall form beaker with magnetic stirring bar. Since the analysis method is based on concentration, volume transfer need not be quantitative, but sample dilution must be avoided as much as possible. Add three or four drops of methyl red indicator solution and acidify with the nitric acid solution to a pale pink endpoint while the stirring bar is rotating. Fill the reference electrode chambers with the appropriate filling solutions if the solution levels are low. Rinse and towel dry the electrode surfaces and immerse the electrodes in the sample solution. Maintain a stirring rate which gives thorough solution mixing. Turn on the ion meter and place controls in the millivolt (MV) readout setting. Allow the millivolt reading to stabilize by coming to a constant value or a net change of 0.1 MV in no less than ten seconds. Record the millivolt reading. Repeat this procedure for each sample solution to be analyzed and for the chloride calibration solution. Chloride content is determined from the millivolt readings using either the calibration curve on page 10 or equation on page 9 by

calculating the difference in IMV readings between the standard and the unknowns.

4. Method of Calibration. The condition of the chloride selective-ion electrode, reference electrode, reference electrode filling solutions, and the presence of interfering substances such as bromide, iodide, fluoride, sulfide, cyanide, and hydroxide can cause deviations in the sample millivolt reading. The electrode response slope will remain constant, however. The calibration curve and equation are based on the constant electrode response slope and the use of a known concentration chloride calibration solution. For the curve and equation shown, the electrode response slope is -56 millivolts per decade (a tenfold change in concentration). Note that this requires a different calibration curve for electrodes with a different response slope.

Use of the standard calibration method requires the preparation of a chloride calibration solution and determination of the electrode response slope. The chloride calibration solution may be prepared from reagent grade sodium chloride in deionized water or from actual sample solutions. Preparation using reagent grade sodium chloride allows easier selection of the calibration solution concentration. Preparation of this solution has been explained above. Preparation using actual sample solutions requires titration with silver nitrate as explained below to determine the calibration solution concentration. The electrode response slope may be acquired from the electrode manufacturer or may be determined by preparation and analysis of known chloride solutions covering at least a tenfold concentration range. By plotting the initial millivolt reading versus chloride concentration on semi-logarithmic graph paper, the electrode response slope (per decade) may be determined from the resulting straight line.

5. Silver Nitrate Titration. This titration may be used for chloride analysis to determine the electrode response slope or for verification of other chloride concentrations. This method is the reference for the standard calibration method.

Using the 50 ml pipet, obtain an aliquot for titration with the 0.01 N silver nitrate solution. Pipet the 50 ml sample into a clean, dry high form electrolytic beaker. Add three or four drops of methyl red indicator solution and acidify to a pale pink endpoint. Prepare the electrodes for use by filling, cleaning, and drying them. Immerse the electrodes in the sample solution, stir, and allow the millivolt reading to stabilize as above. Record this initial millivolt reading (IMV) and start the titration by adding silver nitrate solution in 0.2 ml increments. Allow the millivolt reading to stabilize after each addition and record the millivolt reading or change in millivolt reading between additions. The titration endpoint occurs at the greatest change in millivolt reading. An example of the determination of titration endpoint follows:

<u>Titrant Volume (ml)</u>	<u>MV</u>	<u>ΔMV</u>	<u>Δ^2MV</u>
4.0	220.5		
		9.6	
4.2	230.1		+ 7.0
		16.2	
4.4	246.3		+10.3
		26.5	
4.6	272.8		- 3.8
		22.7	
4.8	295.5		- 9.8
		12.9	
5.0	308.4		

The endpoint is located where Δ^2MV equals zero. This may be determined graphically or by linear interpolation using one point on either side of zero as shown below:

<u>Volume (ml)</u>	<u>Δ^2MV</u>
4.4	+10.3
4.6	- 3.8

$$\Delta V = 0.2 \text{ ml}$$

$$\text{Endpoint} = 4.4 \text{ ml} + 0.2 \text{ ml} \left(\frac{10.3}{10.3 + 3.8} \right) = 4.4 \text{ ml} + 0.146 \text{ ml}$$

$$\text{Endpoint} = 4.55 \text{ ml}$$

Accuracy of the method allows determination of the endpoint to the nearest 0.05 ml. Calculation of weight percent chloride in the concrete follows:

$$\text{Wt. \% Chloride} = \frac{\text{Wt. Chloride}}{\text{Wt. Concrete}}$$

$$\text{Wt. Chloride} = (\text{Titrant volume})(\text{Titrant normality})(\text{Chloride molecular weight})(\text{Aliquot factor})$$

$$\text{Aliquot factor} = \frac{500 \text{ ml}}{50 \text{ ml}} = 10$$

$$\text{Chloride molecular weight} = 35.453 \text{ g/mol}$$

$$\text{Wt. concrete} = 30.00 \text{ g}$$

$$\text{Titrant volume} = V \text{ (ml)}$$

$$\text{Titrant normality} = N \text{ (mol/l)}$$

$$\text{Wt. \% Chloride} = \frac{(35.453)(10) \text{ VN} \left(\frac{1}{1000 \text{ ml}}\right)}{30.00} \quad (100\%)$$

$$\text{Wt. \% Chloride} = 1.182 \text{ VN \%}$$

$$\text{ppm Chloride} = 11820 \text{ VN}$$

$$\text{pounds/ton Chloride} = 47.28 \text{ VN}$$

6. Calculations. Determination of chloride concentration may be accomplished by use of an equation of the following form:

$$C_X = C_S (10^{\Delta E/S})$$

C_X - unknown solution concentration

C_S - standardizing solution concentration

ΔE = $IMV_X - IMV_S$ - difference in millivolt readings

S - electrode response slope (millivolts per decade)

For the case shown graphically:

$$C_X = 500 (10^{\Delta E/-56}) \text{ ppm}$$

STANDARD CALIBRATION CURVE

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NO. 340-L310 DIETZGEN GRAPH PAPER
SEMI-LOGARITHMIC - 3 CYCLES X 70 DIVISIONS

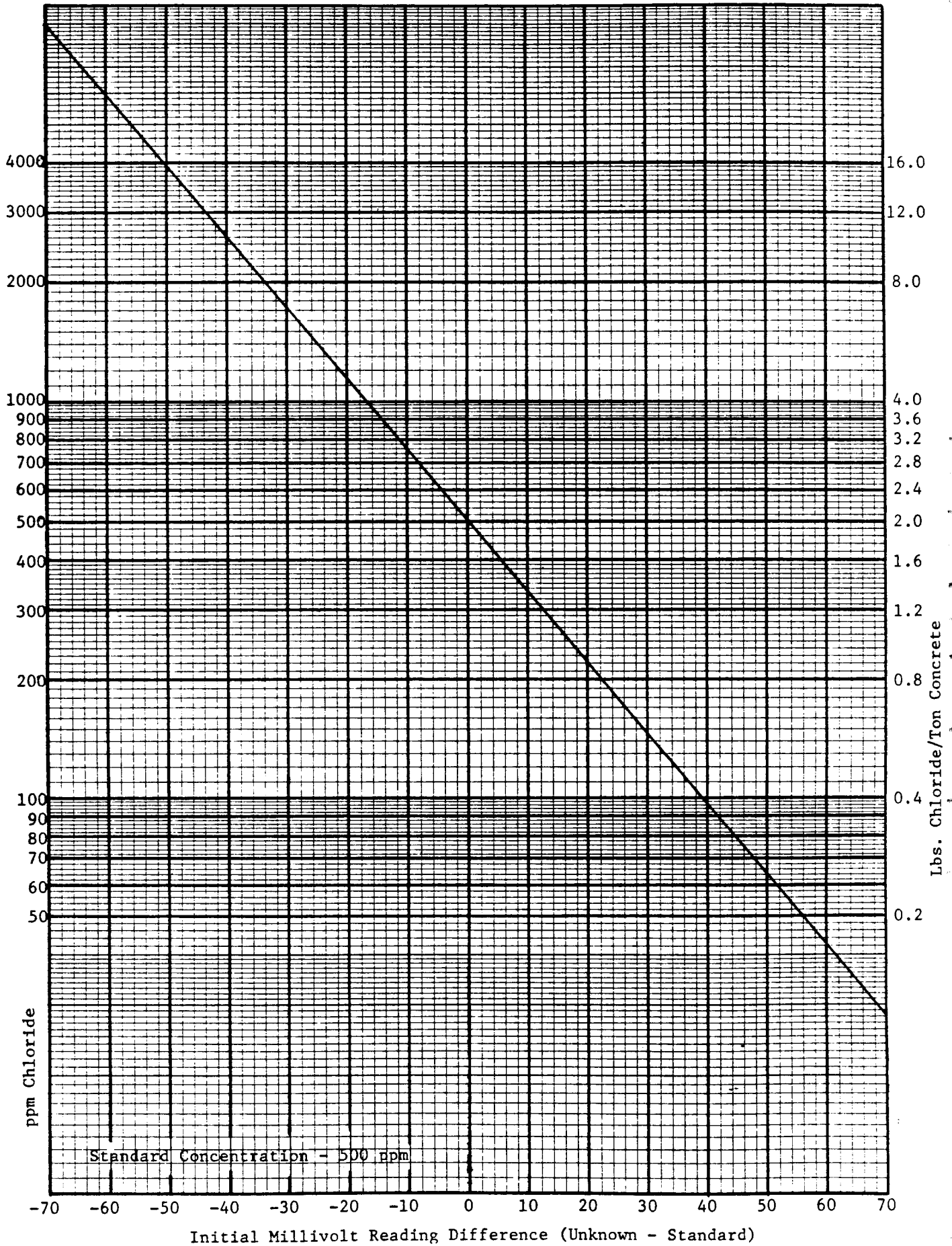


TABLE 1

REPEATABILITY OF SILVER NITRATE TITRATION

<u>Sample Source - Laboratory Number</u>		<u>Titration Results (ppm Chloride)</u>	
Potter Co.	A83330134	402	407
Potter Co.	A83330136	637	637
Potter Co.	A83330136	614	614
Potter Co.	A83330136	880	898
Donley Co.	A83330176	366	366
Donley Co.	A83330176	342	342
Donley Co.	A83330176	419	437
Donley Co.	A83330176	402	390
Nolan Co.	A83330193	112	106
Donley Co.	A83330176	844	839

TABLE 2

REPEATABILITY OF WATER DIGESTION AND ANALYSIS

<u>Sample Source - Laboratory Number</u>		<u>ppm Chloride</u>	
		<u>Run 1</u>	<u>Run 2</u>
Potter Co.	A83330136	638	626
Potter Co.	A83330136	466	484
Potter Co.	A83330137	289	295
Donley Co.	A83330176	366	342
Donley Co.	A83330176	429	396
Orange Co.	A84330029	555	555
Orange Co.	A84330029	649	655
Orange Co.	A84330029	319	277
Orange Co.	A84330029	271	248
Howard Co.	A84330004	1380	1300

TABLE 3

COMPARISON OF KNOWN ADDITION RESULTS

<u>Sample Source - Laboratory Number</u>	<u>ppm Chloride</u>	
	<u>Titration</u>	<u>Known Addition</u>
Hall Co. A84330078	460	775-815
Motley Co. A84330079	340	520
Motley Co. A84330079	225	315-345
Motley Co. A84330079	155	360
Motley Co. A84330079	950	1380

TABLE 4

STANDARD CALIBRATION USING PREPARED STANDARD

<u>Sample Source - Laboratory Number</u>	<u>ppm Chloride</u>	
	<u>Titration</u>	<u>Standard Calibration</u>
Hall Co. A84330078	160	155
Hall Co. A84330078	225	210
Hall Co. A84330078	390	370
Hall Co. A84330078	460	370
Motley Co. A84330079	950	990
Motley Co. A84330079	340	370
Motley Co. A84330079	225	255
Motley Co. A84330079	155	200
Johnson Co. A84330149	300	300
Johnson Co. A84330149	405	400
Johnson Co. A84330149	250	275
Johnson Co. A84330149	275	340
Johnson Co. A84330149	175	215
Hutchinson Co. A84530160	565	600
Hutchinson Co. A84530160	1170	1100
Hutchinson Co. A84530160	260	310
Hutchinson Co. A84530160	75	80

TABLE 5

STANDARD CALIBRATION USING TITRATED SAMPLE

<u>Sample Source - Laboratory Number</u>	<u>ppm Chloride</u>	
	<u>Titration</u>	<u>Standard Calibration</u>
Potter Co. A83330134	955	1000
Potter Co. A83330134	400	360
Potter Co. A83330134	400	390
Potter Co. A83330135	480	445
Potter Co. A83330136	625	630
Potter Co. A83330136	485	485
Potter Co. A83330136	410	370
Potter Co. A83330136	880	860
Potter Co. A83330136	900	830
Potter Co. A83330136	465	460
Potter Co. A83330136	635	615
Potter Co. A83330136	535	595
Potter Co. A83330136	915	960
Potter Co. A83330136	830	860
Potter Co. A83330137	340	335
Potter Co. A83330137	1095	1135
Potter Co. A83330137	295	285
Potter Co. A83330137	275	260
Potter Co. A83330137	215	190
Potter Co. A83330137	280	285

TABLE 6

ATOMIC ABSORPTION RESULTS

<u>Sample Source - Laboratory Number</u>		<u>Titration</u>	<u>ppm Chloride</u>	
			<u>AA-100 ml Preparation</u>	<u>AA-200 ml Preparation</u>
Young Co.	A83330106	515	550-640	
Orange Co.	A84330029	83	110-230	
Young Co.	A83330106	875	865-880	
Orange Co.	A84330029	125	240-280	
Howard Co.	A84330004	745	720-740	
Orange Co.	A84330029	1320 (1000+)	965-985	
Young Co.	A83330106	210	225-265	190-240
Howard Co.	A84330004	300	315-370	280
Young Co.	A83330106	435	460-610	415-420
Orange Co.	A84330029	655	710-765	665
-	-	0	0-90	
Johnson Co.	A84330149	205	295-365	
Johnson Co.	A84330149	300	330-390	
Johnson Co.	A84330149	405	425-470	
Johnson Co.	A84330149	250	270-340	
Johnson Co.	A84330149	275	340-385	
Johnson Co.	A84330149	175	225-260	
Hutchinson Co.	A84530160	380	435-445	
Hutchinson Co.	A84530160	565	620	
Hutchinson Co.	A84530160	1170 (1000+)	980	
Hutchinson Co.	A84530160	260	300	
Hutchinson Co.	A84530160	75	100	
Hutchinson Co.	A84530160	135	175	

TABLE 7

ACID DIGESTION RESULTS

<u>Sample Source - Laboratory Number</u>	<u>ppm Chloride</u>	
	<u>Water-Soluble</u>	<u>Acid Digestion</u>
Randall Co. A83330129	475	625
Randall Co. A83330129	531	802
Randall Co. A83330127	957	1215
Orange Co. A84330029	77	165
Orange Co. A84330029	65	140
Orange Co. A84330029	555	710
Orange Co. A84330029	652	710
Orange Co. A84330029	298	400
Orange Co. A84330029	260	378

TABLE 8

REFLUX METHODS COMPARISON

<u>Thimble</u>	<u>Sample Wt</u>	<u>ppm Chloride</u>
Paper	15 g	315
Paper	30 g	235
Glass	15 g	295
Glass	30 g	260