

VALIDATION OF A METHOD FOR THE EXTRACTION AND QUANTIFICATION OF WATER-SOLUBLE CHLORIDE IN CEMENT BY ION CHROMATOGRAPHY

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Abstract:

Chloride is a corrosive anion that can attack steel and other metal embedded materials in concrete structures leading to its degradation. Chloride in concrete may come from the materials used for making concrete such as cement. Hence, it is important to have a reliable method for determining chloride in cement, in this case the water-soluble chloride which is representative of chloride that may pose corrosion risk. In this study, ASTM C1218/C1218M-20 was used as a guide for sample extraction and the water-soluble chloride was later quantified by ion chromatography. Validation of this method from extraction to instrumental determination was conducted by assessment of the linear range, detection limit, precision, and trueness. It was found that the method was suitable for the determination of water-soluble chloride content in cement.

Keywords: water-soluble chloride; cement; method validation

1. INTRODUCTION

Concrete is a composite construction material consisting of a filler and a binder. Cement paste (cement + water) acts as the binder, while aggregates serve as the filler [1-2]. One of the major degradation mechanisms of concrete is the corrosion of reinforcing steel bars (rebars). Chloride is one of the deleterious species of reinforced concrete [3,6]. The mechanism by which it corrodes the rebar is based on the destruction of the protective thin layer of steel due to the changes in pH. It is usually caused by the thermal transformation products of calcium oxychloride salts. This action is collectively referred to as chloride penetration [4,7].

Chloride may be introduced into the concrete via internal and external sources. Internal sources include inherently chloride-containing mixing-water, cement and aggregates, while external sources come from the surrounding environment. Since it may affect the structural integrity of

excessive levels, it is crucial to test the concrete and its primary ingredients for their chloride content. This is to assess the condition of concrete cover around reinforcement, and forecast the corrosion risk of reinforced concrete where chlorides penetrate [6].

On the basis of how they are tightly held in the material, chloride may be present in two states - chemically bound and free ions. As only the latter primarily influences the corrosion process, the free chloride ion content must be determined to assess risk of corrosion. In essence, the free ions are the ones that can be extracted by water. For this reason, they may also be referred to as the water-soluble chloride [5].

Regulatory bodies have set the maximum permissible level of chloride in concrete. For instance, the American Concrete Institute (ACI) has set the maximum water-soluble chloride content in concrete at 0.06 - 1.00 percent by weight of cement, depending on the type of concrete [8]. Meanwhile, the European Standards (EN 206-26) has a recommendation of 0.1-0.4 percent by weight of cement, depending on the type of concrete [9].

A reliable and accurate analytical method is essential to support this regulation. There are already existing methods used for quantification of water-soluble chloride from the American Society of Testing Materials (ASTM), American Association of State Highway and Transportation Officials (AASHTO), and International Union of Laboratories and Experts in Construction Materials, Systems and Structures (RILEM) [10-11]. They differ in the extraction conditions and quantitation methods. Potentiometric titration, Volhard method, and Ion Chromatography are some of the analytical techniques that can be utilized.

In this study, a method for extraction and quantification of water-soluble chloride in cement was developed and subsequently validated. ASTM C1218/C1218M-20 was used as the main guide for the extraction procedure. Specifically, the objectives of the study are as follows: (1) to harmonize the extraction procedure used in the

laboratory and the next steps in sample preparation prior to instrumental determination, and (2) to validate the extraction procedure and ion chromatographic method to assess its suitability for water-soluble chloride determination in cement.

2. METHODOLOGY

2.1 Materials and reagents

All solid chemical reagents are analytical reagent (AR) grade. Type 1 water was used as diluent to standard solutions and mobile phase and as an extracting solvent.

Calibration stock standard solution used was Supelco Certipur Anion multi-element standard II with 1000 mg/L chloride concentration. Calibration solutions were prepared following the instrument working range of 0.25 - 12.0 mg/L with at least 6 concentration points. The spiking standard solution of 2126 mg/L Cl⁻ was prepared from solid potassium chloride.

Eluent solution or mobile phase was 8.0 mM sodium carbonate (Na₂CO₃)/1.0 mM sodium bicarbonate (NaHCO₃), prepared by dilution of Dionex AS14A eluent concentrate (0.8 M sodium carbonate Na₂CO₃/0.1 M NaHCO₃). The mobile phase was filtered in cellulose nitrate 1.0 μm membrane filter using a vacuum filtration system.

The ordinary portland cement samples (grayish fine powder) were obtained from various local cement plants.

2.2 Sample extraction

The ASTM C1218/C1218M-20 Standard Test Method for Water-Soluble Chloride in Mortar and Concrete [10] was used as a reference for method development of the sample extraction procedure. The general procedure involved weighing 10 g of cement sample, followed by the addition of 50 mL of Type 1 water and boiling the mixture for not more than 5 minutes to extract the water-soluble chloride. Four different conditions (see Table 1) were studied to know the effect of 24 h standing, washing, and dilution to the amount of chloride extracted. All mixtures were filtered using Whatman #42 filter paper and dilutions were made to obtain a 100 mL solution.

2.3 Instrumental determination

Chloride quantification was performed using a Dionex IonPac AS14A analytical column (4 x 250 mm) with Dionex IonPac AG14A guard column (4 x 50 mm) on a Dionex ICS-1000 Ion

Chromatography System. The ion chromatograph is equipped with an isocratic pump, a chemical suppressor and conductivity detector. The instrument conditions used (Table 2) were the same as that already established by the laboratory for the analysis of chloride in water. The standards and samples were manually injected with 0.45 μm acrodisc syringe filter. The chloride ion was eluted 4.4 minutes after sample injection.

Table 1: Different conditions employed for extraction of water-soluble chloride after boiling

Treatment	Sample preparation conditions		
	stand 24 h	washing	dilution
A	Yes	Yes	Yes
B	No	Yes	Yes
C	No	No	No
D	Yes	No	No

Table 2: Ion chromatographic conditions employed for chloride determination

Parameter	Value
Pump flow rate	0.90 mL/min
Suppressor current	50 mA
Cell temperature	30 °C
Injection volume	1 mL
Run time	15 minutes

2.4 Volhard titration method

For the comparison of ion chromatography and argentometric chloride titration, the cement sample was prepared by following ASTM C1218. To the cement water extract, 3 mL of (1:1) HNO₃ was added, followed by 3 mL of 30% hydrogen peroxide. After standing for 1-2 minutes, the solution is heated to near boiling then cooled.

For back titration, 5.00 mL of 0.025 N AgNO₃ was added to precipitate the chloride as silver chloride. Afterwards, 3 mL of benzyl alcohol was added and 2 mL of ferric ammonium sulfate indicator. The unreacted silver ion was titrated with 0.025 N NH₄SCN.

2.5 Method validation studies

Validation of the extraction method and ion chromatographic analysis was performed by using the Eurachem Guide [12] as a reference. Linearity and working range and detection limit was already established in the ion chromatography system for water analysis. Hence the calibration standards were prepared by considering these already established parameters. For repeatability assessment, two cement samples with different chloride

concentrations were used. Since there is no available certified reference material, the trueness of the method was assessed by spiking the sample at around 100% level with 2126 mg/L Cl⁻ which was prepared from solid potassium chloride. The concentration of the laboratory prepared spiking solution was confirmed by ion chromatography.

3. RESULTS AND DISCUSSION

3.1 Effect of different sample preparation conditions

In the initial studies, two ordinary portland cement samples were used to determine the effect of different sample processing conditions after boiling the cement-water mixture on the extracted chloride. ASTM C1218 requires the sample to stand for 24 hours prior to filtration and instrumental determination. Treatment A and D follow the ASTM method in the sense that the sample was allowed to stand for 24 h prior to filtration. Treatment B and C was included in the study to know if the additional solvent used for washing and thereafter dilution will affect the chloride values significantly.

The results in Table 3 show that the different processing conditions after boiling have a significant effect on the obtained chloride values. Samples that were allowed to stand for 24 hours and were diluted afterwards had the lowest chloride concentration while those samples that were filtered after cooling down to room temperature had relatively higher chloride extracted. The final volume after extraction has a great influence on the calculated amount of chloride. For Treatment C and D, the final volume after extraction is less than the original amount of water added (water absorption capacity differ per cement sample) hence this reduction in volume after extraction caused the higher chloride values than Treatment A. Additional amount of water for washings has no effect on Treatment A since the cement has already hardened after 24 hours thereby no additional chloride can be extracted. But for Treatment B, there is a possibility for additional extraction from the washing solvent for the quantitative filtration and dilution hence results for Treatment B are higher compared to Treatment A wherein both employ the washing and dilution step. These results show that the extraction and final sample preparation steps prior to injection in the ion chromatography system have a significant effect on the chloride values. Hence, one can only make a good comparison of results if similar preparation steps were followed.

For consistency in the sample preparation workflow for routine laboratory analysis, the extraction procedure that was followed in the method validation study was Treatment A. The

chloride value obtained by this method was comparable to the acid-soluble chloride content of the cement sample.

Table 3: Effect of different extraction conditions on the water-soluble chloride by ion chromatography

Treatment	Sample 1		Sample 2	
	Average Cl (mg/kg)	%RSD (n=7)	Average Cl (mg/kg)	%RSD (n=3)
A	62.1	2.5	54.1	1.9
B	96.7	1.1	107.6	4.6
C	122.5	6.3	100.5	3.7
D	102.2	2.4	72.3	1.7

3.2 Comparison of ion chromatography and Volhard titration results

The results of ion chromatography were compared with the results obtained by Volhard titration. Using a representative water-extract sample (Sample 1, Treatment B), Volhard titration was performed by following the procedure described in 2.4. The titration results showed an average chloride value of 94.2 mg/kg (%RSD=4.63). There is a good agreement between ion chromatography and Volhard titration results.

Although the results are comparable, the ion chromatography method offers the advantage of being able to detect lower chloride concentrations. Through instrumental determination, operator error in visual endpoint detection during titration is eliminated, removing this bias during chloride determination.

3.3 Method validation results

The suitability of a method is assessed by evaluating various figures of merit which include but are not limited to the following: linear working range, method detection limit, precision, and trueness. The method must pass certain analytical requirements, as shown in Table 4, to consider it fit for the intended purpose.

The maximum permissible level set for water-soluble chloride in concrete is 60 mg/kg. This means beyond this level the chloride may trigger degradation of concrete. Those cement products that contain chloride concentrations below this regulation limit are said to conform to this standard specification. In order to come up with a correct and sound conformity assessment of cements based on their chloride content, a method capable of detecting chloride concentration way below this regulation limit must be in place.

Linear working range is the interval over which the method provides results with an acceptable

uncertainty. The ion chromatography system has an already established working range of 0.25 - 12.0 mg/L. This was based on linear regression analysis and residual plots.

Table 4: Summary of method performance characteristics for water-soluble chloride in cement determination by ion chromatography

Parameter	Acceptance criteria	Experimental Value
linear range (mg/L)	0.25 - 12	0.25 - 12
method detection limit (mg/kg)	60	11
repeatability (%RSD)	5.3 (100 mg/kg)	2.54 (62.1 mg/kg, n=7)
		2.74 (75.2 mg/kg, n=7)
trueness by spiking (% recovery)	90 – 107 (100 mg/kg)	95.5 – 105.5 (100 % spiking level; n=4)

Method detection limit (MDL) is the lowest concentration of the analyte that can be detected by the method at a specified level of confidence. MDL was assessed by analyzing 11 blank samples that underwent the whole analytical procedure. The calculated average chloride concentration and standard deviation (s) was 7.38 and 4.06 mg/kg, respectively. Corrected standard deviation was computed and found to be 3.52 mg/kg. This was multiplied by the factor '3' (as suggested in the Eurachem Guide [12]) to finally determine the MDL which was found to be 11 mg/kg. This is way below the 60 mg/kg acceptance criteria.

Precision is a measure of how close the results are to one another. This can be assessed through the percent relative standard deviation (%RSD). A low %RSD indicates a good agreement of data with one another. Two samples, seven replicates each, were analyzed using the method under repeatability conditions. The %RSD were calculated as 2.54 and 2.74% for sample 1 and 2, respectively. These values passed the 5.3% acceptance criteria at 100 mg/kg concentration level.

Trueness is an expression of how close the mean of an infinite number of results is to a reference value. This was assessed through the percent recovery of spiked samples. The percent recoveries ranged from 95.5 - 105.5%. This is within the 90-107% limit at 100 mg/kg concentration level.

In summary, the method passed the requirements for the four mentioned method

validation parameters, as shown in Table 4. Hence, the method is suitable for the analysis of water-soluble chloride in cement.

3.4 Application of the method to various cement samples

The validated method was used to determine the water-soluble chloride content of different ordinary portland cement samples (mostly Type 1) that are either produced locally or supplied by various cement suppliers. As shown in Table 5, all the cement samples have chloride values that are below the regulatory limit.

Table 5: Water-soluble chloride content of different cement samples from local cement plants and cement suppliers.

Cement sample	Water-soluble chloride (mg/kg)
1	62.1
2	54.1
3	84.2
4	37.7
5	33.2
6	40.2
7	56.8
8	49.4
9	50.3
10	77.6

4. CONCLUSIONS

It was demonstrated in this study that different sample preparation procedures after hot water extraction of the cement would give different chloride values. Hence, only when similar extraction procedures are followed we can expect a good comparability of results. The water-soluble chloride content varied greatly with treatment. Treatment A, which is consistent with ASTM C1218, is the chosen method for the extraction of water-soluble chloride in cement. This was the sample preparation method used in the method validation.

Based on its performance characteristics, the method is suitable for the determination of water-soluble chloride in cement. Linear working range was from 0.25 - 12 mg/L. The method detection limit (MDL) was found to be 11 mg/kg. Method precision (repeatability) was below the 5.3 %RSD acceptance criteria. Method trueness by recovery was within 90-107% requirement.

For further validation, the method can be tested using a certified reference material. Also, other figures of merit such as intermediate precision,

selectivity, among others, should be assessed to further evaluate the method.

5. SUMMARY

The laboratory used ASTM C1218 method to come up with the final procedure for the extraction of the water-soluble chloride in cement. The method involved boiling the cement sample in water and allowing it to stand for 24 h prior to filtration and dilution. Afterwards, the extracted chloride ion was quantitated using ion chromatography. The performance characteristics of this method were assessed and was found to be fit for use in a routine chemical testing laboratory.

6. REFERENCES

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