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Generalization of the possibility of eliminating the filtration step in the determination of acid-soluble chloride content in cement and concrete by potentiometric titration

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Abstract

In this work, it is demonstrated that it is possible to eliminate the filtration step in the determination of the acid-soluble chloride content of cement and concrete by potentiometric titration, irrespective of the method used for detecting the end-point of the titration. Extensive analytical results are presented corresponding to several types of cement and to a broad range of chloride concentrations in concrete. Some requirements to avoid errors in such analytical determinations are discussed.

Keywords: Chloride; Cement; Concrete; Corrosion; Potentiometric titration

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1. Introduction

The accurate determination of the chloride (Cl^-) content of concrete and its raw materials is an important issue in relation with quality control and durability of reinforced concrete structures. This explains the special attention that it has received from many researchers and institutions, by proposing improved methods of analysis [1–3] or by carrying out round-robin tests to assess the accuracy, reproducibility and repeatability of results obtained by different laboratories in these analytical determinations [4–9].

Recently, it was proposed an experimental procedure for the analysis of acid-soluble chloride content in cement, mortar and concrete by potentiometric titration [3], which avoids the filtration step habitually performed in such titrations. The procedure was based on the application of the method of Gran [10] of determination of the end-point of the potentiometric titration. This method was included within the panel of trial procedures of an international round-robin test on total chloride analysis in concrete [8], in which it was rated as providing good analytical results. Nevertheless, other methods of end-point detection are far more known and used than the method of Gran [10], mainly in automatic titration systems, thus rendering the findings of Ref. [3] into limited applicability. It has also been reported [6] the successful application of a potentiometric titration without filtration to the determination of the total chloride content of hardened Portland cement paste samples using a microprocessor-controlled automatic titrator.

The main methods for locating the end-point of potentiometric titrations are the following: graphic determinations of the inflection point of the plotted titration curve; the analytical (or derivative) methods based on the calculation of the first or second derivative of the titration curve; or the titration to a fixed known potential corresponding to the equivalence-point [11], besides to the abovementioned Gran's method. The graphic methods are rather tedious and may be considered as less accurate, hence, they are scarcely used. The detection of the end-point through the derivative methods consists in finding the maximum of the first derivative of the titration curve or the null point of the second derivative because these mathematical conditions correspond to the inflection point (maximum slope) of the S-shaped potentiometric titration curve [11]. These derivative methods are the most used in automated titrators and are prescribed also in the ASTM standard for chloride analysis

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in cement and concrete [12]. Finally, the titration to a fixed potential is also used by some laboratories for the determination of Cl^- contents in concrete [13].

In the precedent paper [3], it was proved that Gran's method for locating the end-point of the titration curve allows to obviate the filtration. This particular procedure was considered as the most adequate, taking into account that the presence of solid residues during the titration could eventually modify the titration curve or shift the potential of the equivalence point, due to ionic adsorption [3]. This interference would affect less if the end-point is determined by Gran's method because the relevant potential-volume data pairs are obtained in the past end-point region. The objective of this work is to demonstrate the possibility of eliminating the filtration step in the determination of Cl^- concentrations in cement and concrete by potentiometric titration, irrespective of the method of detection of the end-point. To this end, extensive analytical data are presented, which correspond to several types of cement and to a broad range of Cl^- contents in concrete. The analytical techniques used to determine the Cl^- concentrations are the standard Volhard titration [14–16] and potentiometric titrations using Gran's method and derivative methods for locating the equivalence point. Besides, the potentials corresponding to the equivalence point were determined by linear interpolation of the data corresponding to the potentiometric titration (derivative method) to assess the possibility of titrating to a fixed potential as a suitable analytical procedure in the presence of solid residues.

2. Experimental

2.1. Cement and concrete samples

The analyzed cement samples were provided by several Spanish cement manufacturers, together with their own measured Cl^- contents (Table 1); these analytical results were obtained mainly by X-ray fluorescence (XRF), unless otherwise stated. Powder concrete samples were obtained from cores taken from real structures exposed to a marine environment. Each sample was analyzed at least twice by each of the methods mentioned in Section 2.2. Their reported analytical results are the average of the obtained values, expressed always as percent Cl^- by total sample mass.

2.2. Analytical procedures, equipment and reagents

The Cl^- contents of the samples were determined by the standard Volhard's method [14–16] and by two potentiometric titration procedures without filtration steps using Gran's method and the derivative method for the detection of the end-point, respectively. The experimental procedure, including sample preparations, equipment and reagents, used in the potentiometric titrations was described before [3]. The details for applying the analytical linearization inherent to Gran's method may be found in Refs. [2,3,10]. The procedure for the detection of the titration equivalence point by the derivative method was the same as prescribed by the corresponding ASTM standard [12]; that is, it was not used as an automated titrator. The criterion used for making sure of the stability of the potentiometric readings near the end-point was the following: the data were taken at a rate of one reading each 3 s, and it was considered stable if five equal correlative readings were obtained. From the data sets obtained in these potentiometric titrations, the potential corresponding to the equivalence point was determined by linear interpolation of the potential-reactant volume curve.

Hydrogen peroxide was used to avoid the interference of sulphides present in the blast furnace slag cements [12,14,16]. Two milliliters of a 30% H_2O_2 aqueous solution was added before boiling the nitric acid suspension of these samples. In the case of the potentiometric titrations performed with the derivative method for the detection of the

Table 1
Analyzed Cl^- contents for the cement samples

Type of cement	Denomination following Ref. [17]	Manufacturer's analysis (% Cl^-)	Volhard's method (% Cl^-)	Potentiometric titration, Gran (% Cl^-)	Potentiometric titration, derivative (% Cl^-)
Portland	CEM I 42,5	0.016	0.020	0.017	0.019
	CEM I 32,5	0.011	0.005	0.005	0.007
	BL I 52,5[a]	0.024	0.023	0.022	0.024
Portland with blast furnace slag	CEM II/A-S 32,5R	0.014[b]	0.013	0.013	0.014
Portland with fly ash	CEM II/B-V 32,5R	0.015	0.009	0.009	0.010
Portland with limestone	CEM II/A-L 32,5R	0.032	0.039	0.037	0.040
Blast furnace slag cement	III/A 32,5/SR[c]	0.07[b]	0.071	0.076	0.076
Blast furnace slag cement	III/B 32,5/SR/BC[d]	0.04[b]	0.044	0.045	0.044
Pozzolanic cement	CEM IV/B 32,5R	0.033	0.030	0.034	0.038
Composite cement	BL V/A 22,5[a]	0.015	0.014	0.016	0.016
Calcium aluminate cement	CAC/R	0.008	0.002	0.008	0.011

[a] White cement.
[b] Analyzed by Volhard's method.
[c] Sulfate and sea-water resistant.
[d] Sulfate and sea-water resistant and low-heat cement.

end-point, and for samples with low Cl^- contents, the solution was spiked with 10 ml of a standard 0.015 M NaCl solution before titration to avoid difficulties in determining the equivalence point due to inadequate definition of the titration curve in the surroundings of this inflection point [1,12]. These additions are not necessary if Gran's method is used instead of the derivative procedure for the determination of end-point.

3. Results and discussion

Tables 1 and 2 show the comparative results of the analysis of acid-soluble chloride for the cement samples and the concrete samples, respectively. In the case of the cement samples (Table 1), a good agreement is observed between the results obtained with the three titration methods used in this work: Volhard's titration (VT), potentiometric titration with Gran's method (PTG) and potentiometric titration with derivative method (PTD). The maximum difference between the values reported in the fifth (PTG) and sixth columns (PTD) in Table 1 is 0.004%, while the maximum difference between the values reported in the fourth column (VT) and the fifth and sixth columns (PTG, PTD) is 0.009%. The results obtained by potentiometric titrations correlate also well with the manufacturers' data, mainly obtained by XRF: The maximum difference between the values reported in the third, fifth and sixth columns of Table 1 is 0.008%. In the case of concrete samples (Table 2), also a good agreement is found between the results obtained with the three titration procedures: The maximum difference between the values reported in the second (PTG) and third columns (PTD) is 0.011%, and the maximum difference between the values reported in the first column of Table 2 (VT) and the other two columns is 0.033%. The slightly higher dispersion found for concrete samples is adequately explained, taking into account the much broader range of Cl^- contents of the concrete samples, as compared with cement samples, including concentrations of Cl^- higher than 1%. It is worth noting that the poorest concordance between the results obtained by Volhard's method with those obtained by the potentiometric titrations without filtration and XRF corresponds to the lowest concentrations of Cl^- (see the last cement sample in Table 1 and the first two concrete samples in Table 2). This result is in agreement with the findings of several authors who reported unsatisfactory repeatability and reproducibility [5,8] or insufficient accuracy [6] of the results obtained by Volhard's method at low Cl^- contents.

Table 2
Analyzed Cl^- contents (as percent by concrete mass) for the studied concrete samples

Volhard's method (% Cl^-)	Potentiometric titration, Gran (% Cl^-)	Potentiometric titration, derivative (% Cl^-)
0.017	0.006	0.006
0.026	0.036	0.037
0.058	0.058	0.060
0.084	0.089	0.091
0.134	0.135	0.140
0.206	0.214	0.219
0.463	0.461	0.472
0.630	0.627	0.628
0.835	0.827	0.829
1.050	1.083	1.083
1.555	1.550	1.552

Table 3
Potentials at end-point of titrations (Ag^+ ISE vs. Ag–AgCl reference electrode)

Type of sample	Minimum value (mV)	Maximum value (mV)	Mean value (mV)	Standard deviation (mV)
Cements	224.2	234.0	228.6	2.8
Concretes	220.0	231.8	225.3	2.8

The potentials corresponding to the equivalence point of the potentiometric titrations were calculated by linear interpolation from the potential-volume data pair sets obtained in these tests, after having determined the reactant volume corresponding to the equivalence point by the derivative method. The results obtained are summarized in Table 3. It may be appreciated that the dispersion of the potentials obtained with each type of samples (cements and concretes) is small; the standard deviations are about 3 mV, with maximum differences between results within each series of about 10 mV. It must be taken into account that these potentials correspond to the inflection point of the titration curve, i.e., the point of maximum slope. This slope is of the order of 30 mV/ml with our experimental conditions. Hence, the deviations of about 3 mV may be considered as inducing only small errors in the titration results. It is also interesting to note that the mean potentials measured are very similar for cement and concrete samples, including cements of very diverse nature. This is indicative of the absence of modifications of the titration curve and the absence of shiftings of the equivalence point potential due for instance to ionic adsorptions onto solid surfaces. In this sense, a universal potential for the end-point determination of about 227 mV could be prescribed for the analysis of Cl^- contents in cement and concrete samples, if the experimental conditions are the same used in this work. It must be stressed that this potential value depends on the nature of the ionic selective electrode (ISE), the reference electrode used and also on the history of both electrodes. For instance, the potential of the Ag–AgCl reference electrode is dependent on the composition of the solution in contact with the Ag–AgCl-sensing element, hence, it is sensible to possible contaminations of the inner chamber electrolyte. Hence, laboratories using potentiometric titrations to a fixed potential must determine the optimum value for this potential with their equipment and conditions, and they must check regularly this value, to prevent errors due to the shiftings of this potential. This checking can be performed by obtaining the full potentiometric titration curve (potential-volume data) for concrete samples of known Cl^- contents.

The proposed experimental procedure for the potentiometric titrations [3] includes a previous adjusting of the pH of the suspension, obtained after acid digestion of the sample, to a value of 2. This step is needed to prevent damages to the ISE: The recommended working range of pH for Ag^+ or Cl^- ISE based on solid Ag_2S or Ag_2S–AgCl membranes is from pH 2 to 12 [18]. Another reason for adjusting the pH of the test suspension to 2 is to minimize the risk of ionic adsorption onto the surfaces of the unsolved matter or onto the walls of the glass beaker containing the nitric acid digested suspension. The chemical nature of both types of surfaces, unsolved matter and glass is mainly siliceous. Electrokinetic studies on quartz [19] have shown that zeta-potential values and, hence, the ionic adsorption capabilities of quartz are minimal for pH values near 2. The isoelectric point for amorphous silica [20] was found to lie also between pH 2 and 3. Finally, zeta-potential measurements of cement samples suspended in solutions of different pH indicate that zero potential charge points are located at approximately pH 2 for Portland and blast furnace slag cements and at approximately pH 4 for fly-ash cement [21]. Some errors by defect have been reported [6] in the determination of Cl^- concentrations of hardened cement paste samples by potentiometric titrations performed without adjusting the pH, i.e., at pH values of approximately 0.5.

Taking into account the results presented here, the results of other authors [6] and the preceding considerations, it is demonstrated that it is possible to eliminate the filtration step in the determination of the Cl^- contents of cement and concrete samples by potentiometric titration, independently of the method used for the detection of the end-point (titration to a fixed potential, derivative methods or Gran's linearization approach) and of the experimental setup and procedures (manual titration and data acquisition or use of an automated titrator). In the case of using automated equipment, some care has to be taken to ensure that the size of the drops of reactant is small enough and that the equilibration time of the potential readings is large enough to allow an adequate determination of the end-point. It is also important to adjust the pH of the suspension to a value of about 2–3 before the titration. In any case, it is always advisable to perform periodic checking of the overall performance of the analytical system by testing cement or concrete samples of known Cl^- concentration [2,4,5,7], especially before introducing modifications in the experimental equipment or procedure. The elimination of the filtration may be considered as an important simplification of the overall procedure, with reduction of the equipment and labware used and of the time consumption in these analysis. Another nonnegligible advantage is the decrease of the risk of errors due to losses during filtration or to incomplete washing of solid residues. The only situation that can imply some inconvenience for the potentiometric titrations without filtration is when titrating the samples with high Cl^- concentrations, indicated by rather low potential readings before starting the titration (less than 150 mV indicate Cl^- content higher than 0.5% with the experimental conditions of our work). In this last case, the titration of the whole (nonfiltered) suspension may waste a significant amount of reactant ($AgNO_3$ solution). Nevertheless, this problem may be easily overcome by measuring the approximate volume of the suspension and by taking an aliquot part by pipetting for analysis. The small error due to the uncertainty of the total volume may be considered as irrelevant, taking into account that this high Cl^- content in concrete, $> 0.5\%$ by total mass, represents an excessive concentration from the point of view of reinforcement corrosion in concrete; that is, these high Cl^- contents need not to be known with extreme accuracy. Conversely, highly accurate results are needed in the critical Cl^- concentration range for steel corrosion, i.e., between approximately 0.025% and 0.1% by total mass. The results obtained in this work within this last range may be considered as highly satisfactory for the proposed potentiometric titrations without filtration.

4. Conclusion

From the results obtained in this work, it may be stated that acid-soluble chloride in cement and concrete can be analyzed by potentiometric titration without filtration, irrespective of the method used for the detection of the end-point of the titration. The accuracy and reliability of the results obtained with these potentiometric titrations are similar with that of a laboratory reference procedure, such as Volhard's method, for cements of very diverse nature and for a wide range of Cl^- concentrations in concrete, from 0.01% to 1.5% by total mass.

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