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A further method for chloride analysis of cement and cementitious materials — ICP-OES

S.S. Potgieter [a,*], L. Marjanovic [b]

[a] Molecular Science Institute, School of Chemistry, University of the Witwatersrand, Private Bag X3, PO Wits, 2050, South Africa
[b] Department of Chemistry & Physics, Tshwane University of Technology, Private Bag X 680, Pretoria, 0001, South Africa

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Abstract

This paper describes the novel application of inductively coupled plasma-optical emission spectroscopy (ICP-OES) for the analysis of the chloride content in various South African cements and cementitious materials. Samples were introduced into the plasma as slurries, with and without 5% (v/v) nitric acid. They were agitated in an ultrasonic bath for 10 min to fully disperse and stabilize the slurries. Calibration was performed by using aqueous solutions of reference materials. Measurements were made on a simultaneous SpectroCIROS^{CCD} ICP-OES with side on plasma. The accuracy of the chloride determination was verified by the analysis of certified reference material. The findings of this investigation are compared with results obtained for the chloride content by the standard EN196-2 indirect Volhard titration and potentiometry with an ion-selective electrode (ISE), previously described as the preferred method. The results obtained with potentiometry and ICP-OES of various commercially available cements were comparable.

Keywords: Chloride analysis; OPC; Cementitious materials; ICP-OES; Potentiometric analysis

1. Introduction

The ability to measure chloride in the cement producing and construction industries is of great importance due to an array of reasons. Most importantly is the fact that corrosion in concrete is mainly caused by chloride ion penetration and eventual reaction with reinforcement. This latter reaction causes an increase in the molar volume of the corrosion products compared to that of the reactants and thus leads to spalling of the concrete and often an increase in the corrosion attack. Eventually the load bearing or structural integrity of the concrete structure is affected and it requires (often expensive) repair work. For this reason the allowable chloride level in the final concrete is strictly regulated by certain standard specifications [1].

The current standard method [2] for chloride analysis in cementitious materials calls for a dissolution of the sample in nitric acid, followed by a classical Volhard titration. This procedure is vulnerable when very low concentrations are analysed and is also complicated by a difficult end point detection in coloured sample solutions. Consequently results obtained with the Volhard method, for South African cements and cement raw materials, especially by inexperienced operators, are often erratic and non-reproducible. A variety of procedures for chloride measurements in cement-related materials has been described and compared in the open literature [3–8]. The variability of results obtained with different methods only serves to complicate the matter further, as indicated by Tritthart and Cavlek [9].

In a more recent study [10] a round Robin test was performed, whereby cement was analysed for total and water-soluble chloride content, by 30 laboratories. The ultimate findings were that the Volhard and Potentiometric titration methods of determination gave the most reliable and reproducible results. The samples used did however contain between 0.05 and 0.3% chloride by mass, in comparison with normal South African Ordinary Portland Cement that contains in the

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* Corresponding author.
E-mail address: sanja.potgieter-vermaak@wits.ac.za (S.S. Potgieter).

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Table 1
Operating conditions

Instrumental operating conditions	
Forward power	1600 W
Coolant flow	14 L min^{-1}
Auxiliary flow	1.5 L min^{-1}
Nebulizer flow	0.87 L min^{-1}
Spray chamber	Cyclonic
Nebulizer	Slurry nebulizer (Burgener T 2002)
Wavelength	135.166 nm

order of 0.003%. Potgieter and co-workers [11] reported a comparison between the Volhard titration and several potentiometric titrations and concluded that the superior method of analysis proved to be an acetic acid dissolution followed by a potentiometric titration.

A fast method for the measurement of chloride in South African cement and raw materials, that would yield reproducible and reliable values would not only assist in kiln performance assessments and quality control applications, but also be a major benefit in failure investigations and forensic examinations. This paper will describe an investigation of analysis of various cements and cementitious materials, for their chloride content, using ICP-OES. Analysis of cement by ICP-OES for its major, minor and trace elements with the aid of slurry sample introduction has been proven to be valuable to be employed on a routine basis [12]. Since chloride analysis of cement samples is required on a routine basis for plant control purposes and quality assurance, the novel application of ICP-OES with slurry sample introduction, was assessed. The obtained results were then compared with results obtained on the same samples, using an improved acetic acid dissolution method and an automated potentiometric titration employing a chloride ion selective electrode (ISE) [11], as well as with the standard EN196-2 [2] Indirect Volhard titration method.

2. Experimental procedure

2.1. Procedures investigated

The following methods of analysis were investigated:

2.1.1. Indirect Volhard titration

The standard EN196-2 [2] method of chloride determination was performed on all the samples.

2.1.2. Potentiometric titration

In this approach 5.0002±0.0036 g of the sample of interest was dissolved in 50 mL of acetic acid with a concentration of 4.76 M in a 250 mL glass beaker. The mixture was then boiled for 15 min to ensure dissolution before cooling. After cooling, the wall of the beaker was rinsed with two 10 mL portions of distilled water and 0.35 g of sodium acetate was added to the solution and dissolved. The samples were then titrated potentiometrically with 0.01 M $AgNO_3$ solution. Potentiometric determinations were carried out using a Metrohm 716 DMS Titrino with a chloride ion-selective electrode (ISE). Before commencing with any potentiometric measurements the ISE was conditioned to the titration conditions, with the aid of some standard solutions. For this purpose, the acetate buffer (50 mL of H_2O + 0.5 g $NaCH_3COO$ + 20 mL CH_3COOH) used in the determination was treated with two additions of a 0.1 M NaCl, respectively. The acetate buffer without any chloride additions, as well as the spiked buffer solutions were then titrated, before any of a series of determinations commenced. In all the potentiometric measurements the Ag/AgCl reference electrode was kept in a separate container and connected to the electrochemical cell (analyzing vessel) by salt bridge with KNO_3, without filtration.

2.1.3. Inductively coupled plasma optical emission spectroscopy

Sample preparation was done as described by Marjanovic et al. [12], as well as by weighing approximately 1–2 g of sample accurately, transferring it into a 100.00 ml volumetric flask and adding a 5.00 mL portion of pure HNO_3 to the flask and made up to mark with de-ionized water (Millipore water of 18 MΩ). Complete dissolution of the soluble matter was ensured by exposing it for 15 min to ultrasonic waves. Slurries were analysed for chloride by employing a simultaneous Spectro CIROS^{CCD} ICP-OES with side on plasma. The operating parameters are shown in Table 1. The instrument was calibrated by using aqueous solutions, prepared from a chloride stock solution (prepared from analytical grade NH_4Cl salt).

2.2. Materials

A brief summary of the samples investigated and reagents used in the investigation is given in Tables 2 and 3.

3. Results and discussion

The electrode conditioning and calibration for the potentiometric titirations are illustrated in Fig. 1. The slope of the calibration curve was found to be 55 mV/pCl (close to the theoretical value of 59 mV/pCl derived from the Nernst equation).

The OPC was analysed with standard addition, due to the more precise results obtained with this method of analysis as was pointed out by Potgieter and co-workers [11]. The commercial cement samples, that did contain chloride-based strength enhancers, were analysed without standard additions.

Table 2
Materials used in the investigation

Nature of material	Source
Cementitious	
OPC	Commercially available cement
Cements A–D	Commercially available cements with higher Cl^- contents due to the addition of strength enhancers
Calcareous	
Limestone	Natural
Gypsum (nat)	Natural

Table 3
Chloride concentrations of various cements and cementitious materials as determined by the EN196-2 [2] method, potentiometric titration and ICP-OES [12]

Sample	Chloride concentration (%(m/m))		
	Volhard titration	ISE potentiometric titration	ICP-OES without acid dissolution
Limestone	0.0069	0.0057	0.0078
Gypsum (natural)	0.0029	0.0021	0.0045
OPC	0.0044	0.0027	0.0037
Cement A	0.175	0.161	0.134
Cement B	0.180	0.162	0.130
Cement C	0.170	0.161	0.135
Cement D	0.165	0.162	0.138

The ICP-OES analysis was performed as described by Marjanovic and co-workers [12]. The results are given in Table 3.

The consistently lower results for the chloride concentrations as obtained by ICP-OES with slurry sample introduction, lead to further investigations of the method. It was suspected that a transport phenomenon was responsible for the lower results. This was investigated by the addition of an internal standard that is acid soluble in the silicate matrix. A 100 mg of $Co(NO_3)_2$ $6H_2O$ was added to cement slurries as well as to the aqueous solution (containing 5% (v/v) HNO_3). These were aspirated into the plasma and the intensities obtained were compared. It was concluded that the intensity obtained for Co in cement slurries was approximately 20–22% smaller than those obtained for Co in aqueous Cl^- solutions, as illustrated for one of the samples in Fig. 2.

The results indicate that it is required to aspirate a slurry, in which the acid soluble ions have been liberated from the silicate matrix, to obtain accurate results. Hence, the commercial cements were analysed as acid digested slurries. The results obtained are given in Table 4.

Comparing the results obtained by ICP-OES (acid digestion) and potentiometry, a 2-way ANOVA without replication (as described by Hanratty [13]) shows that $F_{calc} = 1.4 < F_{crit} = 6.0$, which indicates that the variance of the values obtained by the two different methods are not significant.

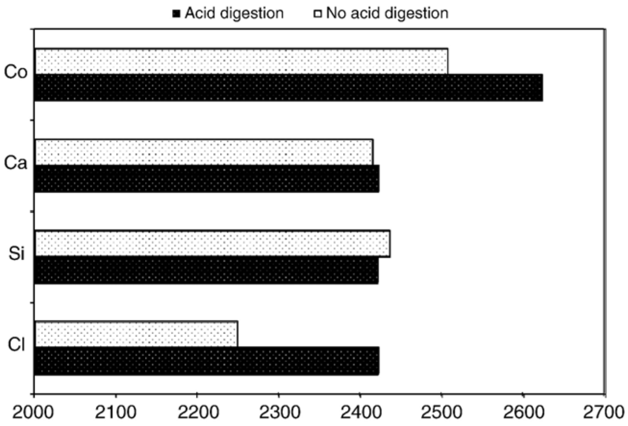

Fig. 2. A comparison of intensities obtained with ICP-OES for a commercial cement introduced into the plasma as a slurry and a slurry with acid digestion.

Finally, the results obtained by ICP-OES were verified by determining the accuracy of the method. Two certified reference materials namely Portland cement X0203 and Enci Portland cement XO208 were analysed, using acid digested aqueous solutions. They were analysed using the method of standard addition since the certified concentrations of Cl^- were very low. The results obtained are presented in Table 5. The results show an excellent correlation with the certified values and confirm the necessity of an acid digestion for chloride analysis.

4. Conclusions

1. Slurry sample introduction resulted in values that were on average 20% lower and acid digested aqueous solutions need to be prepared to release the acid soluble ions from the silicate matrix.
2. Provided that solutions are introduced into the plasma, the method of analysis proved to be both accurate and repeatable.
3. Low chloride cements need to be analysed by means of standard addition.
4. Chloride in cement and cementitious materials can be analysed successfully by ICP-OES with variances of average values, if compared with potentiometric analysis, at an acceptable level.
5. It is therefore recommended to perform ICP-OES analysis for the chloride content of samples on a routine basis since the accurate, repeatable and quick response time will make

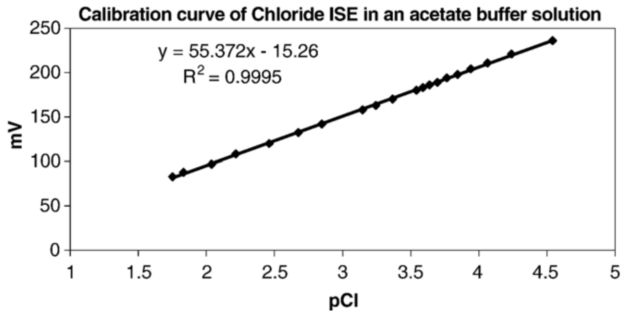

Fig. 1. Calibration curve of ion-selective chloride electrode in an acetate medium.

Table 4
Results for the determination of the Cl^- concentration by ICP-OES in cement and cementitous materials, with acid digestion

Sample	Chloride concentration (%(m/m))	
	Slurry sample introduction	Acid digested introduction
Limestone	0.0078	0.0079
Gypsum(natural)	0.0045	0.0045
OPC	0.0037	0.0035
Cement A	0.134	0.173
Cement B	0.130	0.162
Cement C	0.135	0.187
Cement D	0.138	0.152

Table 5
Accuracy of the slurry method ICP-OES for the determination of Cl^-

CRM analysed	Cl^-concentration obtained (%)	Cl^-concentration certified (%)
CRM × 208	0.032 ± 0.005	0.030 ± 0.003
CRM × 203	0.017 ± 0.002	0.016*

* Recommended value.

this the superior method of all the methods previously investigated by the authors [11].

6. It should be born in mind however, that there are various cements with traditionally low chloride contents, for which extensive and routine chloride analyses are not required. Furthermore, the cost involved with traditional testing is probably lower than that of ICP-OES analysis. However, the cost effectiveness of the new bench-top ICP models, the ease of sample preparation and the speed of analysis could make this the preferred choice if chloride analysis is done on a regular basis.

References

[1] B.J. Addis (Ed.), Fulton's Concrete Technology, Portland Cement Institute, Midrand, South Africa, 1994, pp. 67–70.

[2] SANS 50196-2:2006, (EN 196-2:2005) Methods of testing cement, Part 2: Chemical analysis of cement, Pretoria: SABS, 2006.

[3] R. Jenkins, J.L. De Vries, Practical X-ray spectroscopy (Philips Technical Library, Eindhoven, The Netherlands, 1967).

[4] G. Binder, Incorporation and detection of chlorides in concrete attacked by de-icing salts, ZKG 47 (2) (1994) E60–E64.

[5] M.N. Hague, O.A. Kayyali, Free and water soluble chloride in concrete, Cem. Concr. Res. 25 (3) (1995) 531–542.

[6] E. Proverbio, F. Carassiti, Evaluation of chloride content in concrete by X-ray Fluorescence, Cem. Concr. Res. 27 (8) (1997) 1213–1223.

[7] J.H. Potgieter, A. Horne, Comparison of different methods of chloride determination in cement and cement related materials, S. Afr. J. Chem. 50 (3) (1997) 123–127.

[8] M.A. Climent, E. Viqueira, G. de Vera, M.M. Lopez-Atalaya, Analysis of acid-soluble chloride in cement, mortar and concrete by potentiometric titration without filtration steps, Cem. Concr. Res. 29 (1999) 893–898.

[9] J. Tritthart, K. Cavlek, Determination of total and free chloride in cement paste and concrete, (Second International Rilem Workshop on Testing and Modelling Chloride Ingress into Concrete, Paris, France, 11–12 Sept., 2000, pp. 429–437.

[10] M. Castellote, C. Andrade, Round-robin test on chloride analysis in concrete — part 1: Analysis of total chloride content, Mater. Struct. Chem. Biol. Phys. Technol. 34 (2001) 532–556.

[11] S.S. Potgieter, J.H. Potgieter, S. Panicheva, Chloride measurements in cement and cement-related materials,, Mater. Struct. Chem. Biol. Phys. Technol. 37 (2004) 155–160.

[12] L. Marjanovic, R.I. McCrindle, B.M. Botha, J.H. Potgieter, Analysis of cement by inductively coupled plasma optical emission spectrometry using slurry nebulisation, J. Anal. At. Spectrom. 15 (2000) 983–985.

[13] D. Diamand, C.A. Hanratty, Spreadsheet Applications in Chemistry using Microsoft Excel, Wiley & Sons, U.S.A, 1997.