Determination of chlorine in cement via CaCl molecule by high-resolution continuum source graphite furnace molecular absorption spectrometry with direct solid sample analysis

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ABSTRACT

The use of a new molecule the calcium mono-chloride (CaCl) with absorption band head at 621.145 nm was evaluated in the development of a method for Cl determination in cement by high-resolution continuum source graphite furnace molecular absorption spectrometry (HR-CS GFMAS) employing direct solid sample analysis. Calcium compounds present in cement samples acted as CaCl-forming reagent. Pyrolysis and vaporization curves were established to optimize the atomizer temperature program. The optimum pyrolysis and vaporization temperatures were 1000 °C and 2200 °C, respectively. These values provided higher thermal stability of the CaCl molecule which allows reducing matrix effects and the calibration with aqueous standard solutions in the range of 10–200 ng Cl. Correlation coefficient of 0.995 and a slope of 0.00159 s ng^{-1} were obtained, with a calculated limit of detection of 1.4 ng Cl. Sample masses in the range 0.65–1.05 mg can be accurately weighed and assayed. Commercial cement samples were analyzed by the proposed method and the concentrations of Cl were in the 159–540 µg g^{-1} concentration range. Samples were also analyzed by the Brazilian Association of Technical Norms (ABNT) and results were in agreement at a 95% confidence level (paired *t*-test). Recoveries of Cl added to samples were in the range 101–118% and the relative standard deviations ($n = 12$) were in the 3.4–11.2% interval.

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1. Introduction

According to National Association of Corrosion Engineers (NACE International), the annual cost of corrosion in the U.S. is of $276 billion [1]. In the construction industry sector, chloride is one of the major causes of reinforcement corrosion in concrete structures [2]. Thus that is related to the safety, durability and integrity of concrete structures [3,4]. Maximum allowable chloride contents in cement or concrete are regulated by many international organizations such as American Concrete Institute (ACI) [5], Canadian Standards Association (CSA) [6], Japan Prestressed Concrete Engineering Association (JPCEA) [7], European Committee for Standardization (EN) [8] and Brazilian Association of Technical Norms (ABNT) [9], with the maximum chloride content ranging between 0.02 and 0.14% by weigh of cement, depending on the country regulation. These reports highlight the importance of ensuring a rigorous quality control of chloride concentration in cements.

The determination of chloride in cement and cement-related materials has been performed by different analytical methods and techniques. Among analytical techniques employed for chloride determination in cement are spectrophotometry [10], potentiometric

titration [11], direct potentiometry with ion-selective electrode [12], inductively coupled plasma optical emission spectrometry (ICP OES) [13], ionic chromatography (IC) [14], X-ray fluorescence spectroscopy (XFS) [3] and laser induced breakdown spectroscopy (LIBS) [4]. Most of standard methods are based on potentiometric titration with silver nitrate using a chloride-selective electrode or in the direct potentiometry with ion-selective electrode. These methods require sample pretreatment based on a nitric acid extraction followed by filtration and dilution, which is time-consuming and labor extensive, and may be susceptible to errors and contaminations or interferences caused by other halogens, showing a lack of method selectivity.

These drawbacks can be circumvented by using direct solid sample analysis (DSS) coupled to a high sensitive and selective spectrometric technique used for elemental analysis. Among these techniques the high-resolution continuum source graphite furnace molecular absorption spectrometry (HR-CS GFMAS) is useful to determine non-metal elements (e.g. N, P, S, Cl, Br, F) via absorption of diatomic molecules [15]. These molecules can be formed in the gas phase after the reaction between the analyte and some compound naturally generated inside atomizer or between analyte and some compound previously added to the atomizer (molecule-forming reagent) with the purpose of producing the analyte-containing molecule [16]. Chlorine has been quantified by HR-CS GFMAS using diatomic molecules of SrCl [17], AlCl [18] and

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CaCl [19]. These methods require the addition of 10 μL of solutions containing 10 g L^{-1} Sr [17] or 1 g L^{-1} of Al-Ag-Sr modifier [18] or 20 μg Pd plus 400 μg of Ca [19] as molecule-forming reagents. Considering the high contents of calcium in the cement samples, the development of a reagentless method is promising for generating in situ CaCl. Absorption bands of CaCl around 621.16 nm [20] can be measured within the spectral range of 185–900 nm of the HR-CS GFMAS technique; the molecular bond dissociation energy (409 ± 8.7 kJ mol^{-1}) [21] is compatible to relatively high thermal gas temperatures inside atomizer to allows formation of stable molecular species. Also, the formation of a diatomic molecule from a compound naturally occurring in real samples at high concentration is attractive since extra molecule-forming reagent is not needed.

The purpose of present study was the development of a reliable, simple, reagentless and fast method for determination of chlorine in cement via the monitoring of CaCl by HR-CS DSS-GFMAS.

2. Experimental

2.1. Instrumentation

Analytk Jena ContrAA 700 graphite furnace atomic absorption spectrometer (Jena, Germany) equipped with a xenon short-arc lamp operating in a "hot-spot" mode as continuum radiation source, a high-resolution monochromator and a charge-coupled device (CCD) detector was used for absorbance measurements. Peak volume selected absorbance (PVSA) [22] of 5 pixels was selected for absorbance measurements of CaCl molecule at 621.145 nm. The optimized heating program of graphite furnace is described in Table 1. Pyrolytic graphite-coated solid sampling tubes without a dosing hole and solid sampling platforms transversely heated were used throughput the work. A Sartorius WZ2PW micro-balance (Göttingen, Germany) with a precision of 0.001 mg was used for weighing samples. The platforms were inserted into the graphite furnace using the Analytik Jena SSA 600 automated solid sampler. High-purity argon (99.999%, White Martins, Sertãozinho, Brazil) was used as the purge and protective gas.

The potentiometric titration with silver nitrate using a chloride-selective electrode employed as comparative technique comprised a Corning 450 pH/ion meter (Corning, USA), a Hanna HI 4107 chloride combined ion-selective electrode (Woonsocket, USA) with a Thermo Scientific Orion 900,100 silver/silver chloride (Ag/AgCl) reference electrode (Beverly, USA).

2.2. Reagents and analytical solutions

High purity de-ionized water obtained using a Millipore Rios 5® reverse osmosis and a Millipore Milli-Q™ Academic® deionizer system (resistivity 18.2 MΩ cm, Millipore, USA) was used throughout the work.

A 10% (v/v) nitric acid solution was prepared by proper dilution of the Suprapur® nitric acid (Merck, Germany).

A 100 mg L^{-1} Cl standard solution was prepared by dissolving 0.165 g NaCl (Mallinckrodt, Mexico) in water and making the volume up to 100 mL with water. This solution was properly diluted to prepare a 10 mg L^{-1} Cl solution.

A 10000 mg L^{-1} Ca stock standard solution (Specsol, Brazil) was used to prepare Ca standards.

Single stock standard solutions containing 500 mg L^{-1} Br, F and I were individually prepared by dissolving 0.644 g NaBr, 1.050 g NaF and 0.654 g KI (Mallinckrodt, Mexico), respectively, in water and making the volume up to 1000 mL with water.

All solutions were stored in high-density polypropylene bottles (Nalgene, USA). Plastic bottles and glassware materials were cleaned by soaking in 10% (v/v) HNO$_3$ at least 24 h and rinsed abundantly in deionized water before use.

2.3. Procedure

2.3.1. Sample preparation

Four cement samples acquired at the local market of Araraquara city (São Paulo, Brazil) were analyzed in triplicate by the HR-CS DSS-GFMAS proposed method without any previous treatment.

Samples were also analyzed by direct potentiometry with ion-selective electrode as comparative technique and were prepared in triplicate according to the following procedure: a mass of ca. 2.5 g of cement was accurately weighed and transferred to 250 mL Erlenmeyer flak containing 25 mL of 2% (v/v) HNO$_3$ solution. The mixture was shaken for 10 min at room temperature and then filtered through Whatman No. 42 filter paper. After collecting the filtrate in a 50-mL volumetric flask, the volume was made up with deionized water.

Accuracy of the proposed method was also evaluated by addition/recovery tests. All samples were spiked with 2.0 μL of a 100 mg L^{-1} Cl standard solution in order to obtain a final mass of 200 ng Cl.

2.4. Analytical procedure

The thermal behavior of CaCl molecule was evaluated by means of pyrolysis and vaporization temperature curves established in aqueous medium and cement samples. Absorbance measurements of solutions containing 500 ng Cl (aqueous medium) and 0.5 mg cement (solid medium) were made in triplicate.

After optimizing the heating program, the influence of the nitric acid on absorbance was evaluated by adding different aliquots (0–10 μL) of a 10% (v/v) HNO$_3$ solution to cement samples (masses around 0.6–0.7 mg) previously weighed and deposited on the solid sampling platform.

The influence of variation of mass of Ca on the absorbance of CaCl was evaluated by measuring the signals at following situations: i- 1.0 μL of a 100 mg L^{-1} NaCl solution spiked with 0, 10, 20, 50, 100, 150 and 200 μg Ca; ii- 0.6–0.7 mg cement sample spiked with 0, 10, 20, 50, 100, 150 and 200 μg Ca; iii- 0.6- 0.7 mg cement sample + 2.0 μL of 10% (v/v) HNO$_3$ solution spiked with 0, 10, 20, 50, 100, 150 and 200 μg Ca.

The influence of bromide, fluoride and iodide ions on selectivity was evaluated by measuring the CaCl absorbance after increasing masses (0–5 μg) of each halogen added to 100 ng Cl + 150 μg Ca + 2.0 μL of 10% (v/v) HNO$_3$.

The influence of matrix on sensitivity was evaluated by means of calibration curves (10–200 ng Cl) built in aqueous and solid media. Different aliquots (1.0, 5.0, 10 and 20 μL) of a 10 mg L^{-1} Cl solution were used for aqueous standard calibration. Different masses (0.2, 0.5, 0.9 and 1.1 mg) of a cement sample were employed as solid standards. Each calibration point was measured in triplicate.

The influence of sample size on precision and accuracy was investigated by evaluating the minimum mass of sample to be analyzed in the range of 0.1–1.2 mg of cement sample by increase in increments of 0.1 mg. Each mass interval represents the average weight of three sample masses. The homogeneity factor (H_e) was calculated according to the literature [23].

The reference method described in the NBR 14832 norm from Brazilian Association of Technical Norms (ABNT) was used for

Table 1
Heating program used for Cl determination as CaCl via molecular absorption using HR-CS GFMAS. An argon gas flow-rate of 2.0 mL min^{-1} was used in all steps, except during the vaporization, where the gas flow-rate was 0 mL min^{-1}.

Step	Temperature (°C)	Ramp (°C s^{-1})	Hold (s)
Drying 1	90	20	30
Drying 2	130	20	30
Pyrolysis	1000	300	10
Gas adaption	1000	0	5
Vaporization	2200	2500	7
Cleaning	2450	500	4

comparison purposes [9]. Potentiometric calibration curve for chloride was built up in the 1.10^{-5}–5.10^{-2} mol L^{-1} concentration range containing 0.5 mol L^{-1} KNO_3 supporting electrolyte. All cell potential were measured in triplicate.

After optimization, four commercial cement samples were analyzed using the heating program presented in Table 1. Sample masses around 0.65–0.75 mg were weighed directly onto the platform, followed by addition of 2.0 μL of 10% (v/v) HNO_3. The platform was automatically introduced into the graphite furnace for analysis and determinations were carried out in triplicate.

The limits of detection (LOD) and quantification (LOQ) were determined according to the IUPAC recommendations: $3 \times SD^{blank}/b$ (LOD), and $10 \times SD^{blank}/b$ (LOQ) [24], where SD is the standard deviation for ten blank measurements (using an empty platform) and b is the angular coefficient of the calibration curve.

3. Results and discussion

3.1. Selection of analytical line

Atomic absorption lines of atomic chlorine are located in the vacuum UV region, being the most sensitive line occurring at 138.969 nm [25]. Hence, the determination of Cl by molecular absorption of simple diatomic molecules M-Cl (e.g. AlCl, InCl, GaCl, SrCl) [16] is an interesting alternative. However, limitations of low-resolution AA spectrometers regarding resolution and background correction restricted their use for molecular absorption determinations [16]. These weaknesses were overcome with the introduction of the HR-CS AAS. Among main abilities of the technique are the possibility of resolving rotational fine structures of diatomic molecules and emitting any wavelength between 190 and 900 nm at high intensity. These features allowed the monitoring of diatomic molecules for determination of non-metals such as F [26–28], Cl [17,18], Br [29–32] and I [33]. All these determinations require the addition of molecule-forming reagents. Chlorine has been determined in biological tissues [17], coal [34], food samples [18] and certified reference materials of coal, human hair, pine needles, rice flour, milk and others by HR-CS GFMAS via the monitoring of the AlCl [18], SrCl [17, 34] and CaCl [19] molecules using 10 μL of solutions containing 10 g L^{-1} Sr^{2+}; 1 g L^{-1} Al-Ag-Sr chemical modifier or 20 μg Pd plus 400 μg of Ca, respectively. Besides, the AlCl band observed around 261.42 nm is overlapped by atomic line for cobalt at 261.412 nm [17]. The development of a reagentless method for chlorine determination is attractive. Considering the Ca contents of original cement samples are high enough to induce CaCl formation, extra additions of a CaCl-forming reagent is not necessary. This was then exploited here for Cl

determination in cement by HR-CS DSS-GFMAS. The spectrum of rotational fine structures of CaCl appears between 605 and 635 nm, with maximum at 621.16 nm corresponding to $\Delta v = 0$ vibrational band of the electronic transition $A^2\Pi \rightarrow X^2\Sigma$ [20]. The dissociation energy of the Ca—Cl bond (409 ± 8.7 kJ mol^{-1}) is close to dissociation energies of Al—Cl (502 kJ mol^{-1}) and Sr—Cl (409 kJ mol^{-1}) which are molecules already employed for Cl determinations [17,18].

Shown in Fig. 1 are rotational fine structures of the spectra of CaCl in the vicinity of the absorption line at 621.145 nm obtained from 5 μL of a 100 mg L^{-1} Cl solution as $CaCl_2$ (Fig. 1a) and 0.5 mg of cement sample (Fig. 1b). Analysis of the figure reveals that absorbance spectra of standard and sample are similar, suggesting the feasibility of generating CaCl molecule from cement samples. In spite of the fact that absorbance signals obtained from cement were broader than those observed in aqueous standard, these findings did not impair the use of CaCl proving that the heating program of graphite tube is properly optimized.

3.2. Optimization of the heating program and analytical conditions

Considering the proposed method assay the whole sample, the heating program of graphite furnace must be properly optimized to maximize the elimination of sample matrices. The influence of variations of pyrolysis (400–1600 °C) and vaporization (1600–2400 °C) temperatures on the absorbance of CaCl in aqueous (from 5 μL of a 100 mg L^{-1} Cl solution as $CaCl_2$) and solid (0.5–0.6 mg cement) media was evaluated by means of pyrolysis and vaporization curves (Fig. 2). The behavior of CaCl in aqueous medium was similar to that observed in cement. Considering CaCl remained stable up to around 1000 °C without significant losses of analyte, and the lowest standard deviation of measurements, 1000 °C was chosen as pyrolysis temperature for further studies. Narrow transient peaks, precise measurements and satisfactory sensitivity were obtained at 2200 °C, so this was the vaporization temperature selected for the heating program.

After heating program optimization, influences of the amount of nitric acid and mass of Ca on absorbance were evaluated. The major component of cement is calcium oxide, nevertheless this compound is associated with other oxides as $2CaO \cdot SiO_2$; $3CaO \cdot SiO_2$; $3CaO \cdot Al_2O_3$ and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ [35]. Despite calcium is present in original sample at concentration around 45% (m/m), only small fraction of it is available as effective CaCl-forming reagent. The addition of strong acid (e.g. nitric acid) to cement could favor the liberation of free calcium and improve sensitivity. In fact absorbance increased with increasing amount of nitric acid: when the volume of a 10% (v/v) HNO_3 solution added to sample was varied from 0 to 2.0 μL, absorbance of CaCl increased from 0.16 to a maximum around 0.28. Aliquots higher than 2.0 μL did not
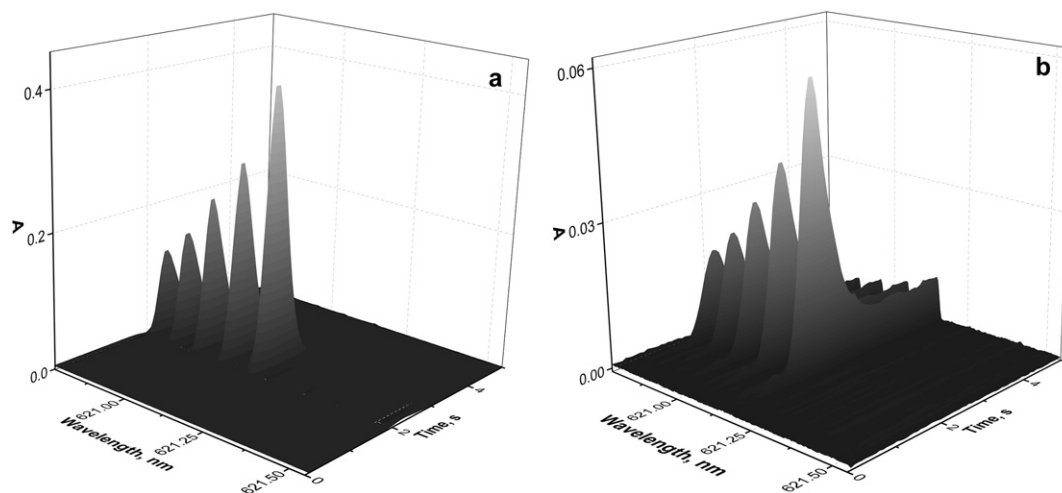

Fig. 1. Time resolved spectrum of the CaCl molecule in the vicinity of most sensitive line at 621.145 nm obtained after vaporization (a) 500 ng Cl + 150 μg Ca, and (b) 0.5 mg of cement.
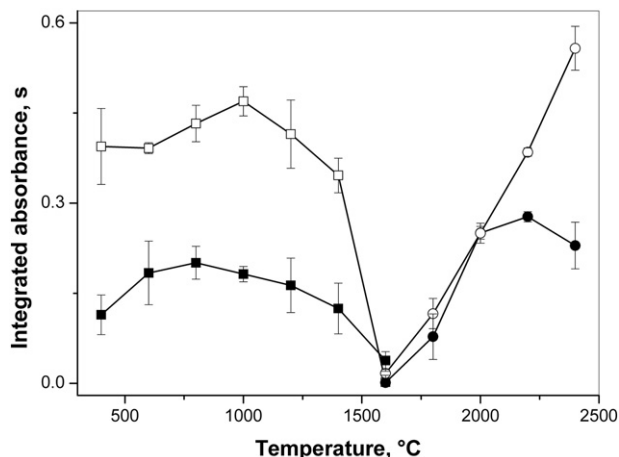
Fig. 2. Pyrolysis (■: solid; □: aqueous) and vaporization (●: solid; ○: aqueous) curves obtained for aqueous medium from (5 μL of a 100 mg L^{-1} Cl solution as CaCl$_2$) and solid medium (0.5–0.6 mg of cement sample).

alter the absorbance significantly, so further experiments were carried out by adding 2.0 μL of acid solution to blanks, standards and samples.

Regarding the influence of variation of mass of Ca on CaCl formation, Fig. 3 shows the importance of adding extra Ca to aqueous solution to induce the CaCl formation. Analysis of this figure reveals that the amount of extra Ca required for maximizing the formation of CaCl in aqueous medium containing 100 ng Cl and 0.6 mg cement is around 150 μg Ca. Figure also revealed that minor fraction of the whole-calcium current in cement acted as CaCl-forming reagent: absorbance was around 0.12 when no Ca was added, showing Ca compounds originally present in cement sample are mostly unreactive. The situation changed when 2.0 μL of 10% (v/v) HNO$_3$ was added to cement: absorbance increased ca. two-fold when compared with the situation with no additions of nitric acid and Ca. Analysis of figure reveals that the presence of nitric acid allowed reaching the maximum absorbance with only 20 μg Ca added. It should be stressed that measurements can be carried out without supplementing Ca and losing the sensibility significantly: absorbance increased ca. 12% when the mass of Ca was varied from 0 to 20 μg. According to the literature, the atomization mechanism of Ca involves the formation of calcium oxides as precursors of atomic calcium [36]. This explains why the better sensitivity can be achieved by spiking calcium despite the high calcium levels of samples. The calcium nitrate is converted to respective oxide easier than the refractory calcium compounds of cement matrices. Further experiments were carried
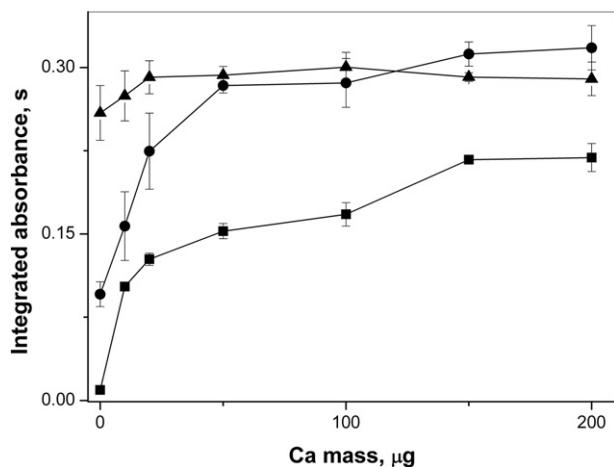
out by adding only 2.0 μL of 10% (v/v) HNO$_3$ to blanks, standards and samples.

3.3. Interference studies

Chloride, bromine, fluorine and iodide form stable molecules with Ca such as CaCl, CaBr, CaF and CaI with dissociation energies of 409, 339, 529 and 284.7 kJ mol^{-1}, respectively [21]. Thus, significant amounts of F, Br and/or I in cement samples may compete with Cl by the molecule-forming reagent. When increasing mass (0–5 μg) of iodide were added to 100 ng Cl + 150 μg Ca, no significant changes in the CaCl absorbance was observed (Fig. 4). This may be explained because the CaCl is more stable than CaI with lower bond energy. Interferences by F and Br were more pronounced than that observed for I. Interference on CaCl formation began at 1 μg Br and F, and reached its maximum for masses ≥2 μg, for which absorbance decreased around 14% and 24%, respectively. Experiments showed that significant interferences were observed for Cl:X (X = Br, F) ratios ≤1:20. However, it should be pointed out that for concentrations of fluoride (240–800 μg g^{-1}) and bromide (6.5–19.4 μg g^{-1}) commonly found in cement [37], no interferes on Cl determinations are expected.

Considering cement reference materials are not commercially available and aqueous standards are the easiest and simplest way to perform calibration, the possibility of using calibration with aqueous standards for direct analysis of cement samples was checked. This was evaluated by means of multiple effects of matrices by comparing the slopes of analytical curves in the 10–200 ng Cl range measured in (aqueous medium) and cement (solid medium), both in presence of 2.0 μL of 10% (v/v) HNO$_3$. Linear correlation coefficients ≥0.995 were consistently obtained. Slopes of curves in aqueous (0.00159 s ng^{-1}) and solid (0.00153 s ng^{-1}) medium were not significantly different at 95% confidence level (*t*-test). These findings showed the optimized heating program of graphite furnace was adequate to eliminate matrices of samples and reduce matrix effects. Thus, calibration with aqueous standards was employed for DSS. The calculated limit of detection (LOD) was of 1.4 ng Cl. For a sample mass of 0.65 mg, the LOD is calculated as 2.1 mg kg^{-1}, which is adequate for quality assurance of cement since it is significantly lower than maximum allowed levels of chloride in cement established by regulatory agencies [5–9].

3.4. Evaluation of sample size and micro-homogeneity

Accuracy and precision of micro-analysis of solid samples depend on sample size and micro-homogeneity. When the sizes are very small, analyzed sample can be inhomogeneous and not representative, while
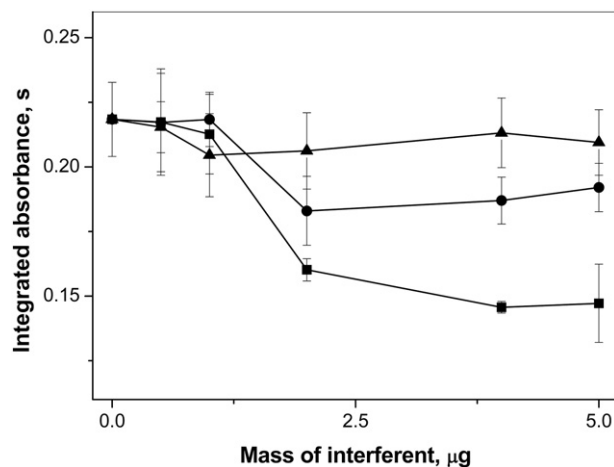

Fig. 3. Influence of mass of Ca on absorbance of CaCl produced from 1 μL of 100 mg L^{-1} NaCl solution (aqueous medium, ■); 0.6 mg of cement sample (solid medium, ●) and 0.6 mg of cement sample + 2.0 μL of 10% (v/v) HNO$_3$ (solid medium, ▲).

Fig. 4. Influence of variation of mass of fluoride (■), bromide (●) and iodide (▲) on absorbance of CaCl using 100 ng Cl + 150 μg Ca + 2.0 μL of HNO$_3$ 10% (v/v) as molecule-forming reagent.

large amount of samples may result in occlusion of analyte [23]. The influence of sample size on accuracy was evaluated by analyzing different masses (0.05–1.25 mg) of a cement sample with known concentration of Cl (158.8 ± 11.9 µg g^{-1}). Fig. 5 shows that accurate results were obtained for sample masses ≥0.65 mg. The micro-homogeneity was evaluated for all interval of mass by calculating the homogeneity factor (H_e) as $H_e = S_H \cdot m^{1/2}$, where S_H is the sampling error and m is the sample mass in milligrams [23]. Sample sizes presenting $H_e < 10$ are considered homogeneous. For the whole interval, masses of samples within the 0.65–1.05 mg interval were considered homogeneous. Nevertheless masses around 0.7 mg were elected for further experiments.

3.5. Determination of Cl in cement

After method optimization, cement samples were analyzed by the DDS HR-CS GFMAS method and by reference method based on potentiometric technique with ion-selective electrode. Results for Cl determinations in commercial samples (Table 2) determined by the proposed method were in agreement with those obtained by reference method at 95% confidence level (paired *t*-test). The concentration of Cl in samples ranged from 158.8–539.9 µg·g^{-1} Cl and the relative standard deviation ($n = 12$) varied from 3.4 to 11.2%. Accuracy was also evaluated by addition/recovery tests. Cement samples were spiked with 200 ng Cl (as NaCl), and recoveries were in the 101–118% interval. These results showed the feasibility of using molecular absorption of CaCl for accurate and precise determination of Cl in cement in a simple, fast and clean way.

4. Conclusions

A new method for Cl determination was developed by using the CaCl molecule with more sensitivity absorption line at 621.145 nm. This molecule presents absorption lines in the visible region of spectrum and high dissociation energy been appropriated for chloride quantifications. The addition of a CaCl-forming reagent was unnecessary since the bulk of sample matrix contains the regent: the addition of only 2.0 µL of a 10% (v/v) nitric acid solution was enough to release calcium ions and/or other compounds more reactive with Cl than compounds originally occurring in cement samples. The sample size and micro-homogeneity studies showed that although relatively large amounts of cement can be collected (cement is not a limited sample), only minute amounts of the test sample are weighed and assayed. The contents of Cl found in selected samples (159–540 µg g^{-1}) are comparable to the other reported values (94–240 mg kg^{-1}) [37] and are in accordance to maximum allowed chloride limits in cement established by existing standards [5–9].
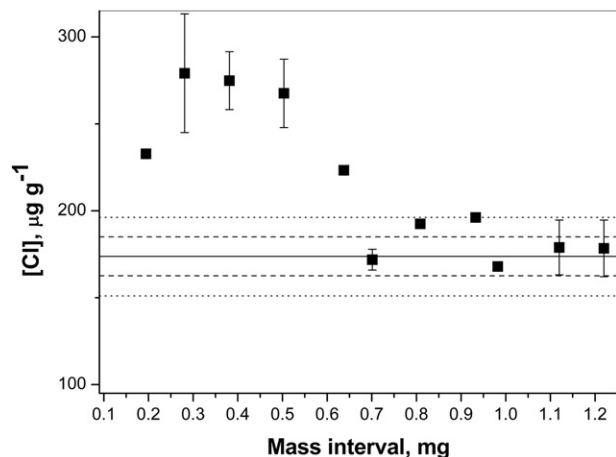
Fig. 5. Influence of sample mass on precision and accuracy of Cl determinations in a cement sample containing known amount of analyte (158.8 ± 11.9 µg g^{-1}).

Table 2
Results (µg g^{-1}, mean $\pm$ SD) for chlorine in cement samples determined ($n = 3$) by the proposed method (DSS HR-CS GFMAS) and by comparative technique (ISE). Recoveries (in %) of 200 ng Cl spikes determined by the proposed method.

Sample	ISE	DSS-HR-CS GFMAS	Recovery
Cement 1	173.8 ± 11.2	158.8 ± 11.9	108
Cement 2	426.5 ± 26.8	394.9 ± 11.9	118
Cement 3	501.5 ± 25.4	539.9 ± 28.9	103
Cement 4	139.3 ± 2.3	146.6 ± 16.4	101

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