Talanta 78 (2009) 81–87

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Determination of strontium and simultaneous determination of strontium oxide, magnesium oxide and calcium oxide content of Portland cement by derivative ratio spectrophotometry

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ARTICLE INFO

Article history:
Received 30 July 2008
Received in revised form 26 October 2008
Accepted 27 October 2008
Available online 5 November 2008

Keywords:
Strontium determination
Portland cement analysis
Derivative spectrophotometry

ABSTRACT

A derivative spectrophotometric method has been developed for the determination of strontium in Portland cement. The method is applied successfully for the simultaneous determination of SrO, MgO and CaO. It is based on the use of Alizarin Complexone (AC) as a complexing agent and measurement of the derivative ratio spectra of the analytes. Interferences of manganese(II) and zinc(II) were eliminated by precipitation. The validity of the method was examined by analyzing several Standard Reference Material (SRM) Portland cement samples. The strontium complex formed at pH 9.5 allows precise and accurate determination of strontium over the concentration range of 1.5–18 mg L^{-1} of strontium. The MDL (at 95% confidence level) was found to be 25 ng mL^{-1} for strontium in National Institute of Standards and Technology (NIST) cement samples using the proposed method.

1. Introduction

As given by the current ASTM Standard Test Methods for chemical analysis of hydraulic cement (C 114) [1], strontium, usually present in Portland cement as a minor constituent, was precipitated with calcium as the oxalate and was subsequently titrated and calculated as CaO, or alternatively correction of CaO for SrO was made, if the SrO content is known. Many analysts and ASTM members have expressed the opinion that (C 114) does not make the distinction between CaO and SrO and the statement referred therein may direct the analyst to not correct the CaO for SrO. Accordingly, the development of a new, direct, sensitive and accurate method for the determination of Sr as a minor constituent in cement is of upmost importance. The objective of this work is to accomplish this.

However, little information is available concerning the determination of Sr in cement matrix, although several works have been published about the determination of strontium. Strontium in presence of higher levels of calcium concentrations has been determined using separation techniques [2–5], many of these methods are not simple and usually they have low selectivity. An atomic absorption spectrometric method for the determination of calcium, magnesium and strontium in soils has been reported [6], for the determination of calcium and strontium, it was necessary to remove silicon.

Derivative spectrophotometry opens up possibilities, not only for increasing selectivity [7–11], but also for increasing sensitivity [12–14]. The scale of this increase depends on the shape of the normal absorption spectra of the analyte and the interfering substances, as well as on the instrumental parameters and the measurement technique (e.g. peak-to-trough or zero-crossing), chosen by the analyst in a given analytical procedure [15–17].

Salinas et al. [18] developed a derivative spectrophotometric method for resolving binary mixtures when the spectra of the components are overlapped. The method is based on the use of the first-derivative of the ratios of the spectra. The absorption spectrum of the mixture is obtained and divided (amplitude by amplitude at appropriate wavelengths) by the absorption spectrum of a standard solution of one of the components (previously stored in a computer), and the first-derivative of the ratio spectrum is obtained. The concentration of the other component is then determined from a calibration graph. Later, the method was extended to the resolution of ternary mixtures in combination with zero-crossing method [19].

Alizarin Complexone (alizarin-3-methylamine-N, N-diacetic acid, AC) is one of the most commonly reagents used for spectrophotometric determination of metal ions [20–23]. No studies have yet been reported demonstrating the solution equilibria of strontium with AC or the use of this reagent for the analytical determination of strontium. As an extension to our previous studies for spectrophotometric determinations of some constituents [24–26] in Portland cement, a rapid and sensitive first-derivative ratio spectrum zero-crossing method is undertaken to determine Sr and its

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doi:10.1016/j.talanta.2008.10.044

closely related cations Mg and Ca in mixtures using Alizarin Complexone as a complexing agent. Specific conditions are applied for simultaneous determination of Sr, Mg and Ca in Portland cement.

2. Experimental

2.1. Chemicals and solutions

A 1×10^{-3} mol L^{-1} stock standard solution of Alizarin Complexone was prepared by dissolving an accurately weighed amount of Sigma (St. Louis, MO, USA) pure grade reagent in absolute ethanol. A 10^{-3} mol L^{-1} stock standard solution of strontium chloride, calcium chloride and magnesium chloride were prepared using the AnalaR grade product. The metal content of the solution was determined by conventional methods [27]. Solutions of perchloric acid, sodium perchlorate and standard sodium hydroxide solution were all prepared from analytical-reagent grade reagents. Solutions of diverse ions used for interference studies were prepared from AnalaR chloride salts of the metal ions and potassium or sodium salts of the anions to be tested.

2.2. Cement samples

National Institute of Standards and Technology (NIST) Standard Reference Materials (SRMs) 1881, 1885 and 1886 were used as the Portland cement matrix in this study. Precautions for handling and use were taken in accordance with the instructions on the NIST data sheet. A complete composition of SRMs samples according to NIST certificates of analysis [28] is given in Table 1. Other samples of ordinary Portland cement (OPC) were supplied by Assiut Cement (Cemex, Egypt).

2.2.1. Dissolution of cement samples

Weigh accurately 0.3–0.4 g of the sample (dried at 110 °C) into a beaker and dissolve it in the minimum volume of hydrochloric acid. Heat to dryness, add 10 mL of HCl (6 mol L^{-1}) to the residue, digest and filter the insoluble residue into a 100 mL calibrated flask and then dilute to volume with doubly distilled water.

2.3. Apparatus

A PerkinElmer (Norwalk, CT, USA) Lambda 35 double beam spectrophotometer was used for ordinary and first-derivative spectral measurements using 1 cm matched quartz cells. The first-derivative spectra were recorded at a scan speed of 240 nm min^{-1}, $\Delta\lambda$ = 5 nm and a slit width of 2 nm. The smoothing and differentiation calculation are based on a least-squares polynomial convulation function using 17 data points.

pH values were measured using a Radiometer (Copenhagen, Denmark) M 201 pH meter equipped with a Radiometer combined glass electrode. The pH meter was calibrated regularly before use with standard buffer solutions and the pH values in water–ethanol medium were corrected as described elsewhere [29].

Table 1
Complete composition of SRM(s) samples according to NIST certificates of analysis [28].

Constituent	1886 (wt%)	1885 (wt%)	1881 (wt%)
CaO	67.43 ± 0.15	62.14 ± 0.14	58.67
SiO_2	22.53 ± 0.06	21.24 ± 0.06	22.25
Al_2O_3	3.99 ± 0.04	3.68 ± 0.07	4.16
Fe_2O_3	0.31 ± 0.01	4.40 ± 0.02	4.68
SO_3	2.04 ± 0.02	2.22 ± 0.02	3.65
MgO	1.60 ± 0.04	4.02 ± 0.10	2.63
K_2O	0.16 ± 0.01	0.83 ± 0.01	1.17
TiO_2	0.19 ± 0.01	0.20 ± 0.01	0.25
Na_2O	0.02 ± 0.01	0.38 ± 0.04	0.04
SrO	0.11 ± 0.01	0.037 ± 0.014	0.11
P_2O_5	0.025 ± 0.010	0.10 ± 0.01	0.09
Mn_2O_3	0.013 ± 0.004	0.12 ± 0.01	0.26
F	(0.01)	(0.05)	0.09
Cl	(0)	(0.02)	0.01
ZnO	(<0.01)	(0.03)	0.01
Cr_2O_3	(<0.01)	(<0.01)	–

Values in parentheses are not certified, but are presented for use as Information Only.

2.4. Procedures

2.4.1. Ordinary spectrophotometry

Transfer an aliquot of a sample solution containing strontium(II) (25–500 μg) and/or magnesium(II) (10–150 μg) and/or calcium(II) (15–250 μg) into 25 mL calibrated flasks. Add 5 mL of 1×10^{-3} mol L^{-1} Alizarin Complexone solution and 5 mL of absolute ethanol to ensure a final ethanol content of 40% (v/v). Adjust the pH to 9.5 using 0.008 M sodium hydroxide, while keeping the ionic strength constant at 0.1 ($NaClO_4$). Dilute to volume with doubly distilled water and record the normal spectrum from 700 to 500 nm against a reagent blank as the reference.

2.4.2. Derivative ratio spectrum zero-crossing method

The stored spectra of Sr–AC complex, Ca–AC complex and their ternary mixture with Mg–AC complex were divided by a standard spectrum of Mg–AC complex. The first-derivative of the ratio spectra were recorded from 650 to 550 nm. In the ternary mixture, the concentrations of strontium and calcium were proportional to the first-derivative divided signals (^{1}DD) at 587 and 612.5 nm (zero-crossing points for Ca/Mg) and 594 nm (zero-crossing point of Sr/Mg), respectively. By the same procedure, the stored spectra of Mg–AC complex, Ca–AC complex and their ternary mixture with Sr-complex were divided by a standard spectrum of Sr–AC complex and the first-derivative of the obtained ratio spectra was recorded. The concentrations of calcium and magnesium in the ternary mixture were proportional to the first-derivative divided signals (^{1}DD) at 594 nm (zero-crossing point of Mg/Sr) and 602.5 nm (zero-crossing point of Ca/Sr), respectively. In this case the concentration of calcium in ternary mixture has been determined twice.

2.4.3. Simultaneous determination of SrO, MgO and CaO in Portland cement

Weigh accurately 0.3–0.4 g of the sample (dried at 110 °C) into a beaker and prepare the sample solution as indicated earlier. Transfer a 25-mL aliquot of the sample solution into a 150-mL beaker. To overcome the presence of calcium in a high level relative to strontium in Portland cement (600:1) add 0.5 mL of 1×10^{-3} mol L^{-1} Sr(II) solution. Add 5 mL of (1:1) ammonium hydroxide solution to precipitate [1] and eliminate the interferences duo to manganese and zinc. Filter into a 100 mL calibrated flask and dilute to the volume with doubly distilled water.

Transfer a 0.5–1.0 mL aliquot of the prepared cement solution into a 25 mL calibrated flask and add 5 mL of AC (1×10^{-3} M). Adjust the pH to 9.5 by the addition of 0.008 M sodium hydroxide. Dilute to volume while keeping final ethanol content of 40% (v/v). Record the absorbance of the solution from 700 to 500 nm against a reagent blank as the reference. Divide the obtained normal spectrum by a standard one for Mg-complex or Sr-complex. Record the first-derivative of the ratio spectrum and measure the amplitudes (^{1}DD) at proper zero-crossing wavelengths as mentioned above. Mg and Ca content in Portland cement were calculated directly using regression equations, only the Sr content was corrected due to the added amount.