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Use of Quinizarin as a Spectrophotometric Reagent for MgO Content Analysis of Portland Cement and Cement Clinker[#]

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Summary. A new direct spectrophotometric method for the determination of magnesium oxide in Portland cement and cement clinker is proposed. The method is based on a reaction with quinizarin (*QUIN*, 1,4-dihydroxyanthraquinone) in ethanol-water (50% v/v) solution at $pH = 9.5$–10.3. Under optimum conditions, the determination of 0.5–3.9 $\mu g \cdot ml^{-1}$ of magnesium is possible. The method is rapid and selective and possesses good accuracy and precision. The analysis of cement materials of variable magnesium content is feasible over the concentration range of 0.85–3.2 $\mu g \cdot ml^{-1}$ Mg; the detection limit is 25.3 $ng \cdot ml^{-1}$ Mg. Under the given conditions, no constituents normally present in Portland cement materials interfer. The procedure was tested by analyzing several standard reference materials and real samples of Portland cement and has been found to give satisfactory results. It has been satisfactorily applied to the determination of magnesium in clay and raw meal.

Keywords. Cement analysis; Mg(II) determination; Sepctrophotometry; Quinizarin.

Chinizarin als spektrophotometrisches Reagens zur Bestimmung des MgO-Gehalts von Portlandzement und Zementklinker

Zusammenfassung. Eine neue Methode zur direkten spektrophotometrischen Bestimmung von Magnesiumoxid in Portlandzement und Zementklinker wird vorgestellt. Sie beruht auf einer Reaktion mit Chinizarin (*QUIN*, 1,4-Dihydroxyanthrachinon) in einem Ethanol-Wasser-Gemisch (50% v/v) bei einem *pH*-Wert von 9.5–10.3. Unter optimalen Bedingungen können 0.5–3.9 μg Mg pro ml bestimmt werden. Die Methode ist rasch und selektiv und zeichnet sich durch hohe Genauigkeit und Präzision aus. Die Analyse von Zementen mit unterschiedlichem Magnesiumgehalt ist über einen Konzentrationsbereich von 0.85–3.2 $\mu g \cdot ml^{-1}$ Mg möglich. Die Nachweisgrenze liegt bei 25.3 $ng \cdot ml^{-1}$ Mg. Unter den gegebenen Bedingungen treten bei gängigen Verunreinigungen im Zement keine Störungen auf. Die Methode wurde an verschiedenen Standards und an reellen Proben getestet und mit zufriedenstellenden Ergebnissen zur Bestimmung von Magnesium in Lehm und Rohmahlgut eingesetzt.

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Introduction

In a dry process cement plant, the production of Portland and other types of cement can be divided into two segments: (a) processing of the raw materials to raw meal/ kiln feed and (b) pyro-processing of the kiln feed to give cement clinker. The raw meal is pre-heated, pre-calcined, and clinkerized by a combination of endothermic and exothermic reactions. Clinker is the basic component in the production of cement which, when combined with other elements, results in the formation of various cement types. Portland cement clinker consists substantially of four crystalline clinker phases in close interpenetrating association. MgO and other foreign oxides are usually incorporated in clinker phases. MgO rich clinker may also contain free magnesium oxide (periclase) which is undesirable. If it is present in substantial amounts, it may cause expansion of concrete, similar to that caused by lime, but more surreptitious. The damage it causes may remain undetectable for years. The magnesium expansion effects are commonly referred to as ''unsoundness'' of the cement. A high proportion of MgO favours the dissolution of C_2S and free lime at higher temperatures and lets C_3S form more quickly. It reduces viscosity and surface tension of the clinker melt and increases ionic mobility [1].

In a cement plant, on-line control of the composition of raw meal is necessary to maintain the composition of the cement within strict requirements. In addition, the composition of the raw materials used has to be traced continuously and constantly. In the cement industry, improvement of the product quality is tantamount to improvement of the chemical composition. The development of new procedures for elemental analysis of cement constituents is desirable because the increasing demand for analytical results requires faster, more selective, and more precise methods. A method for the determination of the magnesium oxide content of cement materials is an absolute necessity. It is the main objective of this work to demonstrate the use of visible spectrophotometry in the determination of magnesium. Selective determination of Mg^{2+} in the presence of Ca^{2+} using common reagents is difficult to perform, and several methods are hampered by the interference from excessive amounts of Ca^{2+} [2–10]. The standard methods for magnesium content analysis of Portland cement are complicated and time consuming [11, 12]. A new spectrophotometric method for the rapid analysis of MgO of cement and raw meal was therefore developped which is superior to other recommended methods in terms of selectivity and sensitivity. The instrument used is cheaper, and the running costs are lower than those for XRF, AAS, or ICP-AES techniques.

Results and Discussion

Acid-base properties of the reagent

The absorption spectra of a $2\times10^{-4}\,M$ solution of *QUIN* in 50% ethanol at various concentrations of $HClO_4$ or NaOH were recorded for various *pH* values (Fig. 1). The reagent yields three coloured acid-base forms in solutions of $pH = 1.5–11.2$: LH_2, LH^-, and L^{2-}. There is a pronounced transformation from the yellow form (LH_2) to the orange red species (LH^-) at $pH = 8.2–9$. The red form is converted to

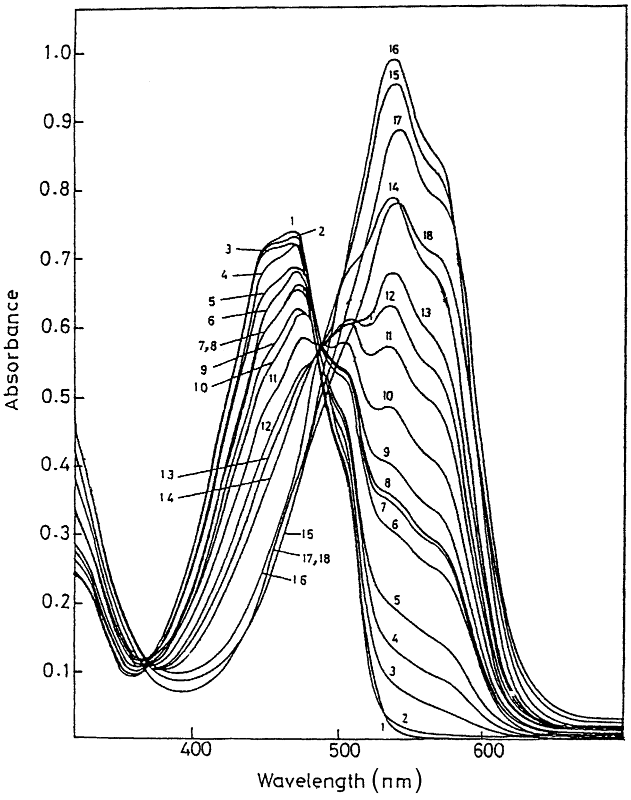

Fig. 1. Absorption Spectra of 2×10^{-4} *M QUIN* at different *pH* values in 50% (v/v) ethanol; *pH*:1) 1.5, 2) 3.8, 3) 6.35, 4) 6.60, 5), 6.8, 6) 7.2, 7) 7.3, 8) 7.4, 9) 7.6, 10) 7.9, 11) 8.1, 12) 8.25, 13) 8.45, 14) 8.7, 15) 10.1, 16) 10.6, 17) 10.9, 18) 11.1

the violet one (L^{2-}) at $pH > 10.8$. Distinct isosbestic points are observed for the particular acid-basic equilibria. The protonation scheme of the reagent indicates that gradual association of protons with the oxygen atoms of the *bis*(hydroxyl) substituents occurs at $pH \leq 10.8$ and ≤ 8.2. The absorbance *vs.* *pH* graphs were interpreted assuming that a particular equilibrium is established under selected conditions [13, 14]. At the working *pH* region and 50% (v/v) ethanol, pK_{a1} (LH_2/LH^-) $= 8.50 \pm 0.03$ and pK_{a2} (LH^-/L^{2-}) $= 10.65 \pm 0.05$ ($I = 0.1$, 20°C).

Complexation reaction of Mg(II) with QUIN

An aqueous Mg^{2+} solution reacts with an ethanolic solution of *QUIN* in alkaline medium (optimum *pH*: 9.5–10.3) to form a blue complex species. The absorption spectrum of the magnesium complex shows an absorbance maximum at 630 nm where the reagent does not absorb. The magnesium complex is formed completely within 5 min of mixing of the reagents and remains stable for at least 4 h.

The complexation reaction of Mg^{2+} with *QUIN* was investigated in 50% (v/v) ethanol over the *pH* range of 8–10.8. The solution spectra were recorded in the presence of an excess of the metal ion, in equimolar solutions, and in the presence of an excess of the reagent. For all solutions investigated, the absorption spectra are analogous and exhibit an absorption band at 630 nm, irrespective of the component ratio (C_L/C_M). The absorption spectra of the Mg-*QUIN* system are shown in Fig. 2.

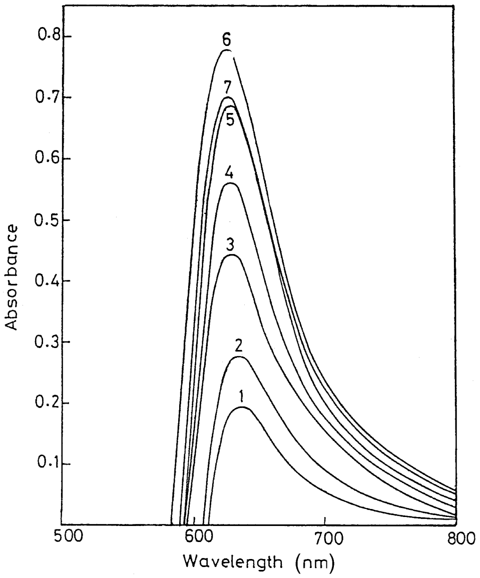

Fig. 2. Absorption spectra of Mg(*QUIN*); $C_L = 2.5 \times 10^{-4}\,M$, $C_M = 1.5 \times 10^{-4}\,M$, 50% (v/v) ethanol; pH:1) 8.05, 2) 8.2, 3) 8.45, 4) 8.7, 5) 9.2, 6) 10.15, 7) 10.65

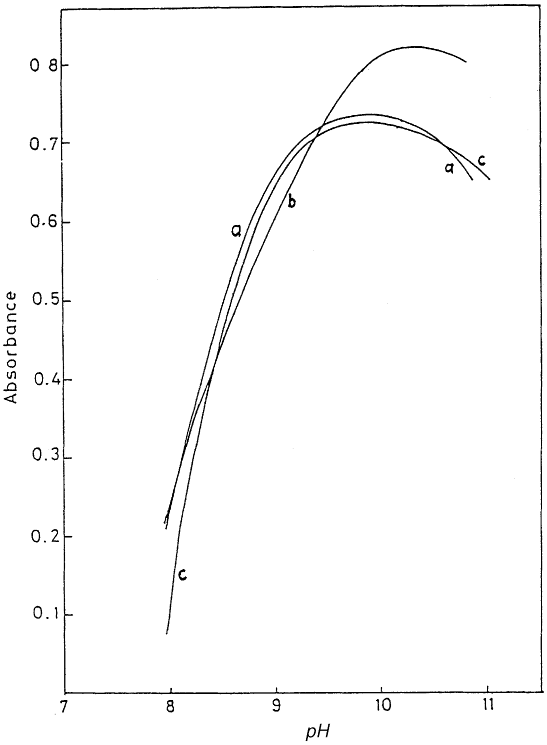

Fig. 3. Absorption *vs.* *pH* graphs for the Mg^{2+}-*QUIN* system at various concentrations of components; $\lambda = 630\,nm$, $I = 0.1\,M$ $NaClO_4$, 50% (v/v) ethanol; a) $C_M = 2 \times 10^{-3}\,M$, $C_L = 2.5 \times 10^{-4}\,M$; b) $C_M = C_L = 2.5 \times 10^{-4}\,M$; c) $C_M = 1.5 \times 10^{-4}\,M$, $C_L = 2.5 \times 10^{-4}\,M$

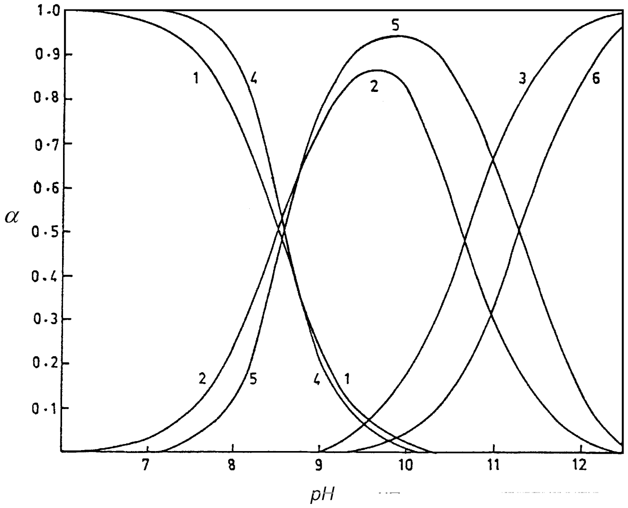

Fig. 4. Distribution curves for the components in the Mg^{2+}-*QUIN* system; 50% (v/v) ethanol, $0.1\,M$ $NaClO_4$; curves 1–3: $C_L = 2\times 10^{-4}\,M$, $\alpha = 1) [LH_2]/C_L, 2)\ [LH^-]/C_L, 3)\ [L^{2-}]/C_L$; curves 4–6: $C_L = 2.5\times 10^{-4}\,M, C_M = 1.5\times 10^{-4}\,M$, $\alpha = 4)\ [Mg]/C_M, 5)\ [MgL]/C_M, 6)\ [MgL(OH)_2]/C_M$

The absorbance *vs. pH* graphs for solutions of different component ratio show the range of formation of the Mg-*QUIN* complex species and indicate a single chelate equilibrium (cf. Fig. 3). The complexation reaction in the *pH* range of 8.2–10.3 is assumed to proceed according to the general equilibrium

$$m\mathrm{Mg}^{2+} + nL\mathrm{H}_x \overset{{}^*K_{11}}{\rightleftharpoons} \mathrm{Mg}_m L_n \mathrm{H}_b^{(2m-q)+} + q\mathrm{H}^+$$

where $b = xn - q$.

The absorbance *vs. pH* graphs for the Mg-*QUIN* system were interpreted using relations derived earlier by *Sommer et al.* [15] and *Idriss et al.* [16] and by the generalized approach described previously [17]. The following equilibria were assumed:

$$\mathrm{Mg}^{2+} + L\mathrm{H}^- \rightleftharpoons \mathrm{Mg}L + \mathrm{H}^+ \tag{1}$$

$$\mathrm{Mg}^{2+} + L\mathrm{H}_2 \rightleftharpoons \mathrm{Mg}L + 2\mathrm{H}^+ \tag{2}$$

By considering the acid-base equilibria of *QUIN* in 50% ethanol and the distribution ratio of the reagent species at different *pH* values, one can assume that the monoionized form of the reagent ($L\mathrm{H}^-$) is the prevalent ligand species in the *pH* range of complexation. From the distribution ratio diagram shown in Fig. 4 it is obvious that the monoligating complex Mg(*QUIN*) attains its maximum abundance at $pH \cong 10$.

The analysis of the ascending part of the absorbance *vs. pH* graphs gives the best fit for equilibrium (1). The existence of this equilibrium was confirmed in solutions containing an excess of one component and in equimolar solutions. For equilibrium (1), in solutions containing excess of *QUIN*

$$\Delta A = \varepsilon_1 C_M - \Delta A \cdot [\mathrm{H}]^q / {}^*K_{11} C_L^n \tag{3}$$

and

$$\log\,[\Delta A/(\varepsilon C_M - \Delta A)] = q \cdot pH + \log{}^*K_{11} + n \cdot \log C_L \tag{4}$$

Table 1. Mean value of equilibrium constant ($\log {}^*K_{eq}$)[a], stability constant ($\log\beta$)[b], and molar absorptivity of the Mg-*QUIN* complex (50% v/v ethanol, $I = 0.1\,M$ $NaClO_4$, 20 °C)

Equilibrium[c]	Constant	log(constant)	Molar absorptivity $l \cdot mol^{-1} \cdot cm^{-1}$
[Mg*L*] [H]/[Mg][*L*H]	${}^*K_{11}$	– 4.69	
[Mg*L*]/[Mg][*L*]	${}^*\beta_{11}$	5.95	4700 ($\lambda = 630$ nm)

[a] From the absorbance *vs. pH* graphs; [b] ${}^*\beta_{11} = {}^*K_{11}/K_{a2}$; [c] charges are omitted

where ε_1 is the molar absorptivity of the Mg*L* complex, *n* is the number of ligand molecules, and *q* is the number of protons liberated during the formation of the complex species. The following equations are valid for equilibrium (1) in solutions with an excess of metal ions:

$$\Delta A = \varepsilon_1 C_L - (\Delta A - \varepsilon C_L) \cdot [\mathrm{H}]^q / {}^*K_{11} C_M \tag{5}$$

$$\log[(\Delta A - \varepsilon C_L)/(\varepsilon_1 C_L - \Delta A) = q \cdot pH + \log {}^*K_{11} + \log C_M \tag{6}$$

with $n = q = 1$.

The metal:ligand ratio and the number of hydrogen ions liberated were further confirmed by the method of *Betteridge* and *John* [18]. The results obtained indicate that only one proton is set free during the complex forming reaction, and equilibrium (1) is predominant. On the other hand, the coordination of a single Mg^{2+} ion with *QUIN* at $pH = 10.0$ is confirmed independently by analysis of $A = f(C_M)$ at $\lambda = 630$ nm using relations given elsewhere [19].

All absorbance *vs. pH* graphs at various concentrations of components have a similarly shaped descending branch above $pH = 10.6$, the shape of which is due to the hydrolysis effect. Side reactions involving the formation of hydroxo complexes prevent the appearence of definite plateaux. The analysis of the descending branch of the graphs for solutions of different component ratio confirms the existence of a hydrolytic reaction (7) of the Mg*L* complex:

$$\mathrm{Mg}L + 2\mathrm{H_2O} \rightleftharpoons \mathrm{Mg}L(\mathrm{OH})_2 + 2\mathrm{H}^+ \tag{7}$$

The stoichiometry of the Mg-*QUIN* complex was further verified by the method of continuous variations. In solutions with $C_o = C_M + C_L = 2.4 \times 10^{-4}\,M$ at $pH = 10$, a component ratio of 1:1 (metal to ligand) was obtained.

The calculated values of the equilibrium ($\log {}^*K_{11}$), the stability constants ($\log \beta_{11}$), and the molar absorptivities of the complex species are given in Table 1.

Effect of diverse ions

In order to assess the usefulness of the proposed method, the effects of diverse ions that often associate with Mg^{2+} were studied. The tolerance of the method to foreign ions was investigated with solutions containing 60 µg of Mg per 25 ml and various amounts of foreign ions. Magnesium was then determined as Mg-*QUIN* under the optimum conditions as described in the Experimental. The tolerance criterion for a given ion was taken as the deviation of the absorbance values by more than ±2% from the value expected for Mg alone. The determination of magnesium as the Mg(*QUIN*) complex was possible in the presence of Al^{3+}, V^{5+}, Mn^{2+}, Fe^{3+}, Hg^{2+}, Mo^{6+}, Cu^{2+}, (about 25-fold excess), Ni^{2+}, Cd^{2+}, Zn^{2+}, Pb^{2+}, Ba^{+2}, Sr^{2+}, Ca^{+2} (~40-fold excess), SO_4^{-2}, Cl^-, Br^-, NO_3^-, ClO_4^-, and PO_4^{-3} (up to about 100-fold excess). The alkali metal ions have no interferring effect on the determination.

Calibration graph, detection limit, and precision

Under the optimum conditions, a linear calibration graph for the Mg-*QUIN* system was obtained up to a concentration of $3.9\,\mu g \cdot ml^{-1}$ of Mg^{2+} with a molar absorptivity of $4.7 \times 10^3\,l \cdot mol^{-1} \cdot cm^{-1}$ at 630 nm. A *Ringbom* plot showed that the optimum concentration range for the determination of magnesium was $0.85–3.2\,\mu g \cdot ml^{-1}$. *Sandell*'s sensitivity of the reaction was found to be $0.88 \times 10^{-3}\,\mu g \cdot cm^{-2}$. The reproducibility of the method was checked by analyzing a series of five solutions with a Mg concentration of $2.4\,\mu g \cdot ml^{-1}$. The relative standard deviation was found to be 0.81%.

MgO content analysis of Portland cement

The potential of *QUIN* as a reagent for direct spectrophotometric determination of magnesium(II) prompted us to explore further the applicability of the method for the determination of MgO in Portland cement and cement clinker. The validity of the method was thoroughly examined. The results of our study indicate that the determination of the magnesium content of cement can be achieved precisely under the optimum conditions (cf. Table 2). Replicate MgO content analyses of SRMs of the US NIST Nos. 1880, 1881, 1886, and 1889 were performed.

In a precision study, five determinations were carried out for each sample. Statistical evaluation of the data indicated good precision of the proposed method which makes its application in the routine analysis of cement possible. Analysis of samples of cement materials containing various proportions of magnesium was feasible over the concentration range of $0.85–3.2\,\mu g \cdot ml^{-1}$ of Mg^{2+}. The detection limit (at 95% confidence level) of the method for a mean of five analyses was calculated as $25.3\,ng \cdot ml^{-1}$. Some results obtained for the analysis of real cement samples and standard reference materials are given in Table 2.

Conclusions

The accurate determination of MgO as a minor constituent in Portland cement is essential. However, there are relatively few methods with the accuracy and selectivity needed to achieve magnesium determination in cement meterials. In this work, a direct spectrophotometric method for the determination of magnesium by use of quinizarin has been studied. The results obtained for a variety of Portland cement materials demonstrate that the proposed method allows precise and accurate determination of the MgO centent of cement. The method has reasonable selectivity and is inexpensive. It saves a lot of time in determining magnesium

Table 2. Application of the proposed method to the direct spectrophotometric determination of MgO in some Portland cement materials

Sample[a]	Statistical term	Magnesium determination (%MgO)
Cement	$\bar{x}$	1.03
	s	1.64×10^{-2}
	95% CL	$\bar{x}\pm0.020$
Clinker	$\bar{x}$	0.99
	s	2.01×10^{-2}
	95% CL	$\bar{x}\pm0.024$
Raw meal	$\bar{x}$	0.63
	s	1.80×10^{-2}
	95% CL	$\bar{x}\pm0.022$
Clay	$\bar{x}$	2.65
	s	2.70×10^{-2}
	95% CL	$\bar{x}\pm0.033$
NIST SRM$_s$ Portland Cement[b]		
SRM 1889	$\bar{x}$	1.37
	s	2.10×10^{-2}
	95% CL	$\bar{x}\pm0.026$
SRM 1886	$\bar{x}$	1.61
	s	2.2×10^{-2}
	95% CL	$\bar{x}\pm0.027$
SRM 1881	$\bar{x}$	2.62
	s	3.14×10^{-2}
	95% CL	$\bar{x}\pm0.039$
SRM 1880	$\bar{x}$	2.63
	s	2.85×10^{-2}
	95% CL	$\bar{x}\pm0.035$

[a] Number of determination for each sample: 5; [b]certified amounts: MgO = 1.38% (1889), 1.6% (1886), 2.63% (1881), 2.61% (1880); $\bar{x}$: mean recovery (%), s standard deviation (%), CL: confidence limit (%); the test solution of the samples investigated contained 5–10 mg of cement material per 25 ml

oxide in cement, clinker, and raw meal samples and could replace the present test methods for magnesium analysis in cement.

Experimental

Apparatus

A Perkin Elmer Lambda 12 spectrophotometer and a Radiometer *pH* meter (M 210) with a Radiometer combined glass electrode were used for measurement of absorbance and *pH*, respectively. The *pH* meter was calibrated regularly before use with standard buffer solutions. All spectrophotometric and *pH*-metric measurements were performed in 50% (v/v) ethanol at 20°C. The *pH* values in water-ethanol were corrected as described elsewhere [20].

Chemicals and solutions

All chemicals used were of analytical grade, and doubly-distilled water (or pure ethanol) was used for the preparation of solutions.

Standard Magnesium Solution: A stock solution ($1\,\text{ml} = 0.49\,\text{mg Mg}$) was prepared using high purity $MgCl_2$ in $0.05\,M$ HCl and standardized against *EDTA*.

Quinizarin (QUIN) stock solution: $10^{-3}\,M$ in ethanol, prepared directly using the purified reagent (Merck).

Other reagents include sodium perchlorate, perchloric acid, and sodium hydroxide standard solutions. Solutions of the foreign ions used for interference studies were prepared using the chlorides sulfates, or nitrates of the metal cations and potassium or sodium salts of the anions to be tested. *pH* adjustment of solutions investigated was performed by the addition of either dilute perchloric acid or sodium hydroxide. The ionic strength was kept constant at $I = 0.1\,M$ $NaClO_4$.

Standard procedure

In a 25 ml calibrated flask, a suitable volume of magnesium solution containing less than 80 µg of magnesium, 6 ml of a $10^{-3}\,M$ *QUIN* solution in ethanol, and 2.5 ml of a $1\,M$ $NaClO_4$ solution are mixed. The *pH* value is adjusted to 10, and the mixture is diluted to volume with doubly distilled water, keeping the ethanol content at 50% (v/v). After thorough mixing, the absorbance at 630 nm is measured against a similarly prepared reagent blank.

Magnesium oxide content analysis of portland cement, clinker, and raw meal

1.0 g of the sample dried at 110°C is weighted accurately into a beaker and dissolved in the minimum volume of hydrochloric acid. After evaporating to dryness, 25 ml of HCl (1+1) are added to the residue. The mixture is digested filtered into a 250 ml calibrated flask, and diluted to volume with bidestilled water. A 2.0 ml aliquot of the solution is transferred into a 25 ml calibrated flask, and 6.0 ml of $10^{-3}\,M$ *QUIN* solution are added. After mixing with 6.5 ml of ethanol and 2.5 ml of $NaClO_4$, the *pH* is adjusted to 10 by adding NaOH solution dropwise and mixing thoroughly after each addition. After dilute to volume and mixing, the absorbance of the solution at 630 nm is measured against a reagent blank of the same *pH* value.

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References

[1] ChaHerigee TK (1981) Burnability and Clinkerization of Cement Raw Mixes. Akademia Books International (abi), India, p 75
[2] Sugawara M, Kambara T (1973) Bull Chem Soc Jpn **46**: 3789
[3] Jiménez MD, Bustamante JA, Marti FB (1975) Anal Chem **47**: 512
[4] Banerjee G, Kanji SK, Mandal S (1976) Z Anal Chem **282**: 47
[5] Sinha BC, Dusgupta S (1978) Talanta **25**: 693
[6] Sinha BC, Roy SK (1980) Analyst **105**: 720; (1982) Analyst **107**: 965
[7] Ying-Quan Z, Lijun-Yi (1982) Analyst **107**: 957
[8] Robiseh G, Rericha A (1983) Anal Chim Acta **153**: 281

[9] Bello López MA, Callejón Mochón M, Gomez Ariza JL, Guiraum Perez A (1986) Analyst **111**: 429
[10] Pal T, Jana NR, Das PK (1992) Analyst **117**: 791
[11] EN 196 Part 2: 1994
[12] Annual Book of ASTM standards, American society for Testing and Materials, 1994, Part C 114–94
[13] Kuban V, Havel J (1973) Acta Chem Scand **27**: 528
[14] Nalimov NV (1963) The Application of Mathematical Statistics to Chemical Analysis. Pergamon Press, London, p 65
[15] Sommer L, Langova M, Kuban V (1976) Coll Czech Chem Commun **41**: 1317
[16] Idriss KA, Seleim M, Saleh M, Abu-Bakr M, Sedaira H (1988) Analyst **113**: 1643
[17] Voznica P, Havel J, Sommer L (1980) Coll Czech Chem Commun **45**: 54
[18] Betteridge D, John D (1973) Analyst **98**: 390
[19] Idriss KA, Saleh MS (1993) Analyst **118**: 723
[20] Douheret G (1967) Bull Soc Chem Fr 1412

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