BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(6), 1945—1946 (1975)

A Fluorometric Determination of Zinc in Portland Cement with 8-Quinolinethiol

Kunihiro WATANABE and Kyōzō KAWAGAKI

Faculty of Science and Technology, Science University of Tokyo, Yamazaki, Noda-shi, Chiba 278

(Received September 20, 1974)

Synopsis. A method for the fluorometric determination of zinc in cement with 8-quinolinethiol is presented. *o*-Phenanthroline and sodium thiosulfate have been found to be useful as masking reagents of interfering ions.

Atomic absorption[1] and polarographic[2] methods, among others, have been proposed in the literature for the determination of the zinc contained in a cement. In the fluorometric determination method of zinc[3] with 8-quinolinethiol previously reported by the present authors in connection with the removal of interfering ions, it was found that 8-quinolinethiol forms a stable complex with zinc and that most of the main constituent elements of a cement except iron do not interfere. In view of these findings, a fluorometric method has been developed for the determination of zinc in cement.

Good agreements were obtained between the results of the present method and those of conventional atomic absorption method.[1] The relative error of this method was from 1 to 5%.

Experimental

Reagents and Apparatus. A stock solution of zinc was prepared by dissolving 1.5286 g of zinc metal (Wako Junyaku Co.) in dilute hydrochloric acid. A 0.2% 8-quinolinethiol solution was prepared by dissolving 0.1 g of 8-quinolinethiol hydrochloride (Dojin Yakka Co.) in 50 ml of 6 M hydrochloric acid. The other reagents used were of an analytical reagent grade. The 8-quinolinethiol solution and chloroform were used for washing some of the reagents.

A Hitachi fluorescence spectrophotometer, Model 203, with a mercury lamp, was used for the fluorometric measurements. A Toa Denpa, Model HM5A, glass electrode pH meter was used for the pH measurements. An Iwaki KM shaker was also used.

Standard Procedure. Put 10 ml of a sample solution containing less than 30 μg of zinc into a beaker. Add 5 ml of a 10% ascorbic acid solution as well as 0.2 ml of a 0.2% 8-quinolinethiol solution (6 M HCl solution).

Dilute to about 50 ml with water, and adjust the pH of the solution to 4.0. Then transfer the solution to a separatory funnel and extract the zinc chelate with 10 ml of chloroform by shaking the funnel for 2 min. Measure the fluorescence intensity of the extract with reference to a 0.2 μg/ml uranine solution.

Results and Discussion

Effect of Diverse Ions. The effects of the main components of a cement on the fluorometric derminations of zinc have been intensively studied. The results are shown in Table 1. Calcium, aluminum, magnesium, sodium, potassium, and silicate ions do not interfere. However a large amount of aluminum forms hydroxides in an aqueous solution of pH 4; therefore, this element must be masked by ascorbic acid. Titanium and chromium do not interfere. Manganese does not interfere when zinc chelate is extracted at pH 4. Iron interferes strongly. Among the minor elements[4] in a cement, nickel, cobalt, copper, lead, and cadmium interfere.

Table 1. Effect of diverse ions

Ions	(mg)	Added	Zn found (μg)
Ca^{2+}	340	$Ca(NO_3)_2 \cdot 4H_2O$	7.6
Mg^{2+}	25	$Mg(NO_3)_2 \cdot 6H_2O$	7.6
Al^{3+}	36	$Al(NO_3)_3 \cdot 9H_2O$	7.6
Na^{+}	1000	NaCl	7.6
K^{+}	1000	KCl	7.6
Mn^{2+}	0.25	$MnSO_4 \cdot 6H_2O$	7.6
Fe^{2+}	0.1	Fe + HNO_3 + 0.1% *o*-phen 3 ml + ascorbic acid	7.5
Cd^{2+}	0.007	Cd + HNO_3 + $Na_2S_2O_3 \cdot 5H_2O$ 1 g	7.9
Pb^{2+}	0.1	$Pb(NO_3)_2$ + $Na_2S_2O_3 \cdot 5H_2O$ 1 g	7.6
Ti^{4+}	0.46	TiO_2 + H_2SO_4	7.6
Hg^{2+}	0.1	$Hg(NO_3)_2$	5.2
SO_4^{2-}	2000	$(NH_4)_2SO_4$	7.6
VO_3^{-}	2	NH_4VO_3	7.4
PO_4^{3-}	1	$(NH_4)_2HPO_4$	7.6
SiO_3^{2-}	20	Na_2SiO_3	7.6

Zn taken: 7.6 μg; pH: 4.0; *o*-phen: *o*-phenanthroline

Masking and Removal of Interfering Ions. The uses of potassium cyanide and *o*-phenanthroline as masking reagents of iron ions were examined. The amount of potassium cyanide has little effect on the fluorescence intensity of zinc chelate. However, because of the use of the masking reagent in an alkaline solution, some ions from hydroxides, thus interfering with the fluorescence intensity. Potassium cyanide was less effective in masking than *o*-phenanthroline. In view of these results, *o*-phenanthroline was chosen as the masking reagent.

The effect of the concentration of *o*-phenanthroline is shown in Fig. 1. The extractability of chelate decreases upon the addition of more than 5 ml of a 0.1% *o*-phenanthroline solution. However, less than 5 ml of *o*-phenanthroline has very little effect on the fluorescence intensity.

The amount of iron ions to be masked by *o*-phenanthroline was also examined. As is shown in Fig. 2, a 5-ml portion of 0.1% *o*-phenanthroline is required to mask 0.3 mg of iron ions.

The procedure used to remove some interfering ions is as follows: Add *o*-phenanthroline and 8-quinolinethiol to the sample solution to form the zinc chelate. Then extract the zinc chelate with chloroform. Repeat the extraction. Combine the organic extracts. To

separate the zinc from the organic phase, shake with a 0.1 M hydrochloric acid solution. In this back-extraction, copper (up to 0.1 mg) and cobalt (up to 0.1 mg) ions remain in the organic phase, but the zinc, lead, cadmium, and nickel are transferred into the aqueous phase. Lead and cadmium react with sodium thiosulfate to form thiosulfate complex ions; therefore, lead (up to 1 mg) and cadmium (up to 10 μg) are masked with sodium thiosulfate. In the case of the coexistence of *o*-phenanthroline, nickel does not interfere up to 50 μg.

Synthetic Sample. For the synthetic sample of cement shown in Table 2, the separation of the chloroform layer from the aqueous layer after the extraction of the zinc chelate was difficult. For quick separation into two layers, a 10-ml portion ethyl alcohol was added to the sample solution.

Determination of Zinc in Cement Samples. In view of the experimental results described above, the recommended procedure for the determination of zinc in cement samples is: Take about 0.25 g of a cement sample, and 0.5 g of ammonium chloride, and add 5 ml of hydrochloric acid to the mixture. Then heat on a steam bath for 30 min, and add 20 ml of hot water to the solution for the complete dissolution of the soluble components of the cement sample. Filter the solution, and wash the precipitate with hot water. Cool the filtrate, and dilute the solution to 250 ml in a volumetric flask.

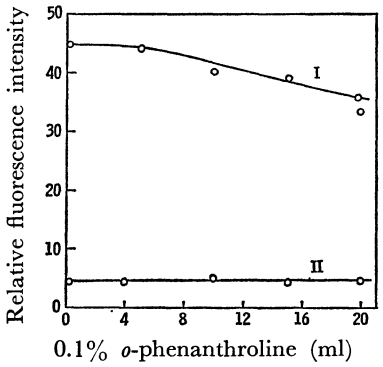

Fig. 1. Effect of amount of *o*-phenanthroline.
0.2% 8-quinolinethiol: 0.2 ml; pH: 4.0;
I: Zn 7.6 μg; II: Zn 0 μg; Wavelength: 365 nm/520 nm

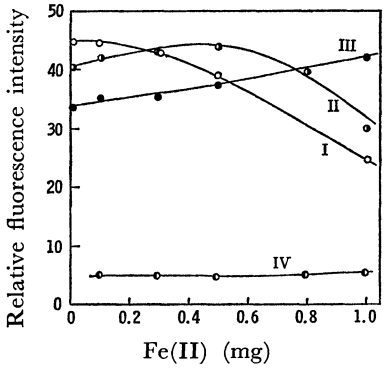

Fig. 2. Masking of Fe(II) with *o*-phenanthroline.
0.1% *o*-phenanthroline (I: 5 ml; II: 10 ml; III: 20 ml; IV: 20 ml)
Zn: 7.6 μg (I, II, III); Zn: 0 μg (IV); Wavelength: 365 nm/520 nm

Table 2. Analytical results of synthetic samples

Sample No.	Zn taken (μg)	Diverse ions (mg)	Zn found (μg)
I	7.6	Al^{3+} 6, Mg^{2+} 3, Ca^{2+} 120, Fe^{3+} 1, Cr^{3+} 0.1, Mn^{2+} 0.1, Ti^{4+} 0.08, Ni^{2+} 0.04, Cu^{2+} 0.04, Pb^{2+} 0.04, SiO_3^{2-} 1, PO_4^{3-} 0.1	7.5, 7.6, 7.5
	3.8		3.8, 4.0, 3.9
II	7.6	Ca^{2+} 240, Mg^{2+} 6, Mn^{2+} 0.1, Al^{3+} 12, SiO_3^{2-} 1, PO_4^{3-} 0.1, Cr^{3+} 0.1	7.6, 7.6, 7.5

Table 3. Analytical results of portland cements

Portland cement	Sample taken (g)	Zn found (%)	
		Proposed method	Atomic absorption method
I	0.2706	0.06_4	0.06_1
II	0.2171	0.04_0	0.04_4
III	0.2143	0.05_8	0.05_8

Pipet a 10- or 20-ml aliquot into a 100-ml beaker, add 5 ml of a 10% ascorbic acid solution, and 5 ml of a 0.1% *o*-phenanthroline solution to each 10 ml of the sample solution and 10 ml of ethyl alcohol. Then dilute the solution to 50 ml, add 0.3 ml of a 0.2% 8-quinolinethiol solution, and adjust the pH to 4. Extract the zinc chelate with 10 ml of chloroform by shaking for 2 min. Put the aqueous phase into a beaker, add 0.2 ml of 0.2% 8-quinolinethiol, adjust the pH to 4, and repeat this extraction twice. Combine the organic extracts. To back-extract zinc chelate from the organic phase, shake with 40 ml of 0.1 M hydrochloric acid for 2 min. Separate the aqueous phase, neutralize with a sodium hydroxide solution, and add 1 g of sodium thiosulfate to the solution. After the complete dissolution of the sodium thiosulfate, add 0.2 ml of 0.2% 8-quinolinethiol, adjust the pH to 4, and extract the zinc chelate with 10 ml of chloroform. Measure the fluorescence intensity with respect to a uranine solution. The zinc content (0— 30 μg) can then be calculated from the calibration curve.

The zinc in synthetic and Portland cement samples was determined by the proposed method. The results are shown in Tables 2 and 3. The present method is rapid and accurate enough for the determination of zinc in cement. The relative error of this method was from 1 to 5% for from 0.01 to 0.1% of zinc.

References

1) H. Ishii, H. Einaga, and M. Numata, *Onoda Kenkyu Hokoku*, **19**, 61 (1967).
2) H. Ishii, H. Einaga, and E. Aoki, *Bunseki Kagaku*, **14**, 149 (1965).
3) K. Watanabe, and K. Kawagaki, *ibid.*, **22**, 581 (1973).
4) H. Ishii, *ibid.*, **17**, 533 (1968).