

Fluorescence Spectrometric Determination of Aluminum(III) Ion in Water Using 4-Chloro-2-phenyliminomethylphenol

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Al(III) ion is usually found in spring water and ground water naturally. It is often found in tap water due to coagulation reagents, such as aluminum sulfate or poly aluminum chloride, used for the water cleaning process. It is also found in teas and kitchen vessels.^{1,2} The toxicity of Al(III) ion in human body has been a topic of interest over the past decades. It can damage various tissue cells in the central nervous system, and it has been suggested that accumulated aluminum in brain tissues is a cause of Alzheimer's disease.³ Therefore, considerable attention has been paid to the development of the quantitative determination of trace amount of Al(III) ion in water.

Several methods have been established to detect the presence of Al(III) ion in water.⁴⁻¹¹ It has been revealed that the absorption spectroscopic method has relatively low detection sensitivity.⁴ However, the fluorescence spectrometric method has been used for the quantitative determination of many organic and inorganic compounds due to its unique high sensitivity. Various organic compounds, such as salicylidene-*o*-aminophenol,⁵ *N*-salicylidene-2-amino-3-hydroxyflurene,⁶ *N,N'*-oxalylbis(salicylaldehydehydrazone),⁷ 2,6-bis[(*o*-hydroxy)phenyliminomethyl]-1-hydroxybenzene,⁸ and other Schiff base ligands,⁹⁻¹¹ have been identified as useful fluorescent reagents for the quantitative determination of Al(III) in water.

In this work, we synthesized a new bidentate Schiff base ligand, 4-chloro-2-phenyliminomethylphenol (Cl-PMP), as shown in Figure 1. Interestingly, Cl-PMP has been found to be useful for the quantitative determination of small amount of Al(III) ion dissolved in tap water, spring water or mineral water.

Experimental Section

Materials and Apparatus. Aniline, 5-chlorosalicylaldehyde and other chemical compounds were obtained from Aldrich and Fluka. IR spectra were obtained using an IR 440

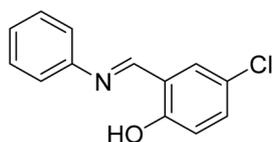


Figure 1. 4-Chloro-2-phenyliminomethylphenol (Cl-PMP).

spectrometer (Shimadzu, Japan) and fluorescence spectra were from a FP-6300 spectrofluorometer (Jasco, Japan). ¹H and ¹³C-NMR spectra were recorded from Mercury 300 (Varian, U.S.A.). Elemental analyses were performed using Valio EL (Elementar, Germany). Mass spectra were obtained using GCMSD-QP5050 (Shimadzu, Japan). The pH of the solutions were measured using 692 pH meter (Metrohm, Swiss). Ultra pure water was obtained using Milli-Q Plus (Millipore, U.S.A.).

Synthesis of 4-Chloro-2-phenyliminomethylphenol (Cl-PMP). To a preheated solution of aniline (1.9 g, 20 mmol) in ethanol (200 mL), was added 5-chlorosalicylaldehyde (3.2 g, 20 mmol) slowly, and the mixture was stirred for 6 h at 60 °C. The resulting orange solution was stored in a refrigerator for 24 h to give yellow crystals. The product was recrystallized from methanol and dried in a vacuum desiccator (Yield: > 85%). Anal. Found: C, 67.34; H, 4.30; N, 6.04%. Calc. for C₁₃H₁₀NOCl: C, 67.40; H, 4.35; N, 6.05%. UV/Vis (ethanol): λ_{max}, nm (ε, M⁻¹cm⁻¹) 226 (4,300), 262 (3,100), 398 (2,600). ¹H-NMR (CDCl₃): δ 6.99 (d, *J* = 8.7, 1H), δ 7.46 (m, 7H), δ 8.56 (s, 1H). ¹³C-NMR (CDCl₃): 118.79, 119.89, 121.16 (two signals), 123.57, 127.33, 129.46, 131.19, 132.85, 159.65, 161.21. IR (KBr, cm⁻¹) 3200 (v, O-H), 1610 (v, C=N), 1580, 1480 (v, C=C), 650-600 (v, C-Cl). Mass (EI): *m/z*: 231 (M⁺), 77 (base).

Fluorimetric Determination of Al(III) Ion. The Al(III) solution was prepared by diluting a 1.0 mM AlK(SO₄)₂·12H₂O standard stock solution. The buffer solution was made using CH₃COOH-CH₃COONa or NH₄OH-NH₄Cl. The solvent was 90% ethanol-water (90/10, v/v). The concentrations of Al(III) solutions for obtaining the calibration line were between 1.0 × 10⁻⁹ and 1.0 × 10⁻¹⁰ M, while that of Cl-PMP was kept at 1.0 × 10⁻⁴ M. The pH of the resulting solution was checked and adjusted using a pH meter. The sample was excited at 397 nm and the fluorescence emission was recorded. The concentration of Al(III) ion was determined from the calibration line at 498 nm in 90% ethanol-water (v/v). The Al(III) ion concentration of each sample was also determined using standard addition method and atomic absorption spectroscopy method for the reliability of the present method. The interfering ion experiments were performed by adding various concentrations of metal ions to 1.0 × 10⁻⁴ M Cl-PMP and 8.0 × 10⁻⁹ M Al(III) ion solutions with NH₄OH-NH₄Cl buffer (pH 10.5).

The stoichiometry between Al(III) and Cl-PMP was determined by plotting the fluorescence intensities at 497 nm with different ratios. The tested molar ratios for Cl-PMP to Al(III) were 0 to 4.0 with 0.25 to 0.5 intervals. The concentration of Cl-PMP was 1.0×10^{-4} M.

In order to maximize the detection limit of Al(III) ion for the samples from various natural sources, pH of the samples was adjusted to 2.0 by the addition of HNO₃. The samples were then incubated between 35 °C to 45 °C for more than 1 hr before fluorescence measurements in order to stabilize the fluorescence intensity.

Results and Discussion

Synthesis of 4-Chloro-2-phenyliminomethylphenol (Cl-PMP). The mass spectrum as well as the elemental analysis corresponds to the formula of Cl-PMP. The IR spectrum shows $\nu(\text{C}=\text{N})$ at 1610 cm^{-1} . ¹H NMR spectrum shows the imine hydrogen at 8.56 ppm. In the ¹³C NMR spectrum, the imine carbon peak is observed at 161.2 ppm. The UV/VIS spectrum shows absorption bands at 226 and 262 nm due to the aromatic groups of Cl-PMP. These results are confirmed by comparing with those from other related Schiff base ligands.¹²

The fluorescence Spectra. The fluorescence spectra of Cl-PMP or a mixture of Al(III) and Cl-PMP measured at different pHs (pH 6.0, 8.0, and 10.5) are shown in Figure 2. The addition of Al(III) ion to a solution of Cl-PMP increases the intensity. It is also seen that the intensity at pH 10.5 is considerably higher than those measured at pH 6.0 or 8.0. The enhanced fluorescence emission in the presence of metal ion can be attributed to the formation of a complex, in which the ligand Cl-PMP is deprotonated. This idea corresponds to a general trend that the fluorescence emission ability of a metal ion-Schiff base complex increases as the ionic character of the metal-oxygen bond is increased.⁹

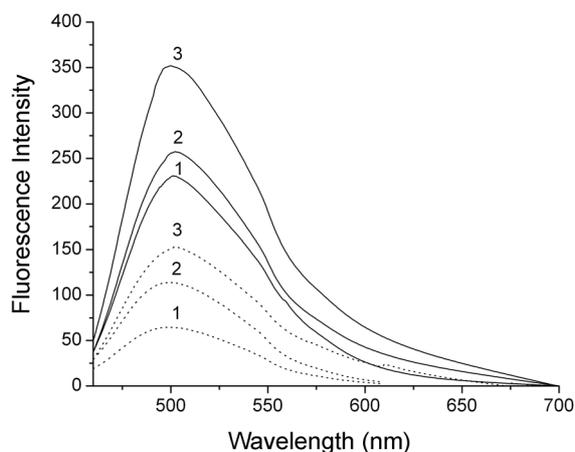


Figure 2. Fluorescence spectra of Cl-PMP (1.0×10^{-4} M) and its complex with Al(III) ion (1.0×10^{-9} M) in 90% ethanol-water. The samples were excited at 397 nm. Dotted line represents the fluorescence spectra of Cl-PMP while solid line does those of Al(III)-(Cl-PMP) complex. 1 represents a spectrum measured at pH 6.0, 2 at pH 8.0 and 3 at pH 10.5.

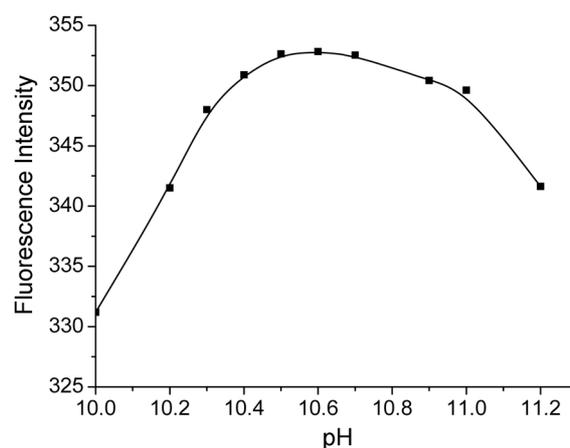


Figure 3. Influence of apparent pHs on the fluorescence intensity of the Al(III)-(Cl-PMP) complex. The samples were excited at 397 nm and the fluorescence intensities were recorded at 498 nm. [Cl-PMP] is 1.0×10^{-4} M and [Al³⁺] is 1.0×10^{-9} M in 90% ethanol solution.

The effect of pH on the fluorescence intensity at 498 nm for Al(III)-Cl-PMP complex is shown in Figure 3. The intensity at pH 10.5 is relatively constant and higher than those measured either below pH 10.3 or above pH 10.9. Therefore, pH 10.5 was selected for the quantitative determination of Al(III) ion in water. It can be suggested that the effective fluorescent species is the complex between Al(III) ion and deprotonated Cl-PMP because the pK_a of phenols are about 10. The decrease of intensity at higher pHs may be attributed to the formation of hydroxides of Al(III).

The effect of ethanol concentration on the fluorescence intensity at 498 nm for Al(III)-Cl-PMP complex is shown in Figure 4. The intensity increases as the concentration increased up to a measured value of 90% aqueous ethanol solution (v/v). Below 70%, the intensity is constant and low. The intensity for concentrations higher than 90% ethanol could not be measured because of the solubility of the aqueous buffer solution and metal ions. The increase in the

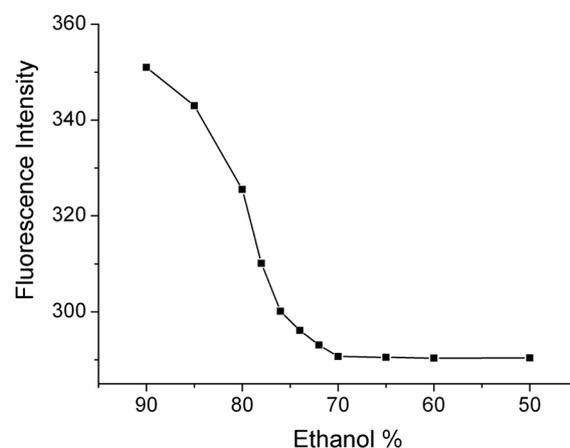


Figure 4. Effect of ethanol concentrations on the fluorescence intensity of the Al(III)-(Cl-PMP) complex. The samples were excited at 397 nm and the fluorescence was recorded at 498 nm. [Cl-PMP] is 1.0×10^{-4} M and [Al³⁺] is 1.0×10^{-9} M at pH 10.5.

Table 1. Effect of foreign ions on the determination of 20 pg/mL of Al(III). The interfering ion experiments were performed by adding various concentrations of metal ion solutions to 1.0×10^{-4} M Cl-PMP at pH 10.5

Ions	Tolerance level (pg/mL)
Na ⁺ , K ⁺ , NH ₄ ⁺ , Hg(II), Rb ⁺ , Pb(II), NO ₃ ⁻ , NO ₂ ⁻ , Cl ⁻ , Br ⁻ , I ⁻ , ClO ₄ ⁻ , K ⁺ , CO ₃ ²⁻	150,000
Sn(IV), Li ⁺	75,000
Ba(II), SO ₄ ²⁻ , Sr(II)	50,000
Mn(II), Hf(IV), SO ₃ ²⁻ , Zr(IV)	25,000
SCN ⁻	10,000
Mg(II), Ag(II), Fe(II), Ca(II), Sb(III), W(VI)	5,000
In(III), Fe(III), Cr(III), Cd(II), Zn(II), Mo(IV), V(V)	1,000
Co(II), Ni(II), Cu(II), Bi(III), tartrate, acetate	100
Ga(III), EDTA, Be(II), citrate	70
F ⁻ , oxalate	40

fluorescence intensity in ethanolic media could be caused by the low solubility of Al(III)-Cl-PMP complex in water, as in the case of other Al(III)-Schiff base complexes reported.⁸

The stoichiometry between Al(III) ion and Cl-PMP calculated from the mole ratio and continuous variation methods was found to be 1:1.8 indicating the formation of [Al(III)-(Cl-PMP)₂].

Determination of Al(III) Ion in Water. The calibration curve for the quantitative determination of Al(III) in water showed a linear relationship in a range of Al(III) ion concentrations between 2.7 and 27 pg/mL with a correlation factor of 0.9997. Below 2.7 pg/mL, the curve was not trustworthy due to its low sensitivity. Various Schiff base fluorescent reagents⁵⁻¹¹ and non-Schiff base fluorescent reagents, such as Morine,¹³ Pontachrome Blue Black R,¹⁴ Eriochrome Red B,¹⁵ 8-hydroxyquinoline-5-sulphonic acid,¹⁶ lumogallion,¹⁷ and bispyrenyl polyether¹⁸ have been examined for the determination of Al(III) ion. The lowest detection limit has

been reported to be 20 pg/mL from the direct fluorescence spectrometric determination of Al(III) ion.^{13c} The detection limit of 2.7 pg/mL in the present method is at least an order of magnitude lower than the other results.

The concentrations within tolerance limit (5%) of various interfering ions on the fluorescence spectrometric determination of Al(III) ion are shown in Table 1. The determination of Al(III) ion is interfered with some positive ions, such as Ga(III) and Be(II), and negative ions such as F⁻, oxalate, EDTA, and citrate. However, the level of interfering ion concentrations is much higher than that of Al(III). Other ions in Table 1 do not interfere noticeably. These results indicate that Cl-PMP is suitable for the determination of Al(III) ion in water, even in the presence of other ions. The tolerance level of this new method to various interfering ions is much better than those of other reported methods.^{7,8}

The amounts of Al(III) ion in various samples were determined by the present fluorescence spectrometric method. The data are listed in Table 2, along with those obtained from standard addition method and atomic absorption spectroscopy (AAS). Table 2 clearly shows that the present method is very useful for the determination of Al(III) ion in various water samples. The bigger error for the present method, compared with standard addition method, could be explained as the matrix effect of samples.

In conclusion, Cl-PMP is a very useful reagent for the fluorescence spectrometric determination of Al(III) ion in water. The samples were excited at 398 nm, and the emitted fluorescence was recorded at 498 nm. The optimized conditions for the fluorimetric determination were obtained in 90% ethanol-water (v/v) at pH 10.5. The present method shows good linear quantitative relations between the concentration and fluorescence intensity within the concentration range of 2.7 and 27 pg/mL Al(III).

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Table 2. Determination of Al(III) in water samples from various sources. The water samples were prepared by adding HNO₃ and incubated for more than 1 h between 35 °C to 45 °C before fluorescence measurements. Results from the fluorescence spectrometric method are shown, together with the values from standard addition method and atomic absorption spectroscopy (AAS) for the comparison

Water samples	Amount found* : ng/mL		
	Fluorescence spectrometric method		AAS
	Calibration curve method (SE; SD)**	Standard addition method (SE; SD)**	
Tap water (Gyeongbuk Yeongcheon)	18.1 (0.07; 0.13)	18.0 (0.04; 0.06)	18
Tap water (Gyeonnam Namhae Changseon Jijok)	16.8 (0.20; 0.34)	16.8 (0.02; 0.03)	17
Mineral water (Chungbuk Choungwon Chojoungli 78-1)	412.5 (1.27; 2.21)	414.8 (0.35; 0.61)	415
Mineral water (Daegu Banyawoul Kwangchun Onchun)	580.9 (1.58; 2.74)	580.2 (0.19; 0.32)	584
Mineral water (Daegu Palkongsan Onchun)	584.7 (0.74; 1.21)	589.6 (0.03; 0.06)	594

*Average of three determinations. **SE: standard error, SD: standard deviation.

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