

This article was downloaded by: [University of California Davis]

On: 18 November 2014, At: 16:08

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Analytical Letters

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/lanl20>

### Fluorimetric Analysis of Aluminum in Diluted Hemodialysis Solutions by Using a Novel Schiff Base

S. Beniz Gündüz<sup>a</sup>, Esra Maltaş<sup>a</sup> & Salih Yıldız<sup>a</sup>

<sup>a</sup> Department of Chemistry, Faculty of Science, Selçuk University, Konya, Turkey

Published online: 13 Dec 2010.

To cite this article: S. Beniz Gündüz, Esra Maltaş & Salih Yıldız (2010) Fluorimetric Analysis of Aluminum in Diluted Hemodialysis Solutions by Using a Novel Schiff Base, Analytical Letters, 43:18, 2892-2904

To link to this article: <http://dx.doi.org/10.1080/00032711003763673>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

## Fluorescence

# FLUORIMETRIC ANALYSIS OF ALUMINUM IN DILUTED HEMODIALYSIS SOLUTIONS BY USING A NOVEL SCHIFF BASE

S. Beniz Gündüz, Esra Maltaş, and Salih Yıldız

*Department of Chemistry, Faculty of Science, Selçuk University,  
Konya, Turkey*

*A spectrofluorimetric method has been developed for trace amount of aluminum(III) by using a novel Schiff base, N,N'-bis(salicylidene)-1,4-diaminobutane (BUTAS), and 4-methyl-2-aminophenol (OAP). Since the aluminum complexes are generally fluorescent, aluminum(III) increases the fluorescence intensity of BUTAS-OAP by formation of Al-BUTAS-OAP complex. The fluorescence of the complex is measured at an excitation wavelength of 410 nm with an emission at 526 nm. Aluminum(III) can be detected within a concentration limit of 0.11–1.62 ppb and the lowest detection limit being 0.07 ppb. The proposed method was applied to diluted hemodialysis solution and spectrofluorimetric data was compared with data of standard pharmacopoeia method.*

**Keywords:** Determination of aluminum; N,N'-bis(salicylidene)-1,4-diaminobutane; Spectrofluorimetric method

## INTRODUCTION

The prevalence of Alzheimer's disease will increase over the next decade with the ever increasing aging population of Western Europe. However, the role played by aluminum as well as other elements, e.g., iron and silicon, either in the aetiology or pathogenesis of the development of this disease remains unclear. Aluminum accumulation in the brain was initially assayed in two groups of patients; first, in postmortem tissue of Alzheimer patients' brains often associated with neurofibrillary tangles and amyloid plaques, and second, in the long term hemodialysis patients treated with aluminum-containing phosphate binders and/or dialysate water containing high levels of dissolved aluminum salts (Croom and Taylor 2001). Considerable evidence also indicated that there was disruption of iron homeostasis in

Received 30 September 2009; accepted 25 October 2009.

The authors are grateful for the financial support provided by the Selçuk University Research Foundation (BAP), Project number: 2005/05101008, and thank Assoc. Prof. Dr. Hamdi Temel, Faculty of Education, University of Dicle, for his valuable contributions.

Address correspondence to S. Beniz Gündüz, Department of Chemistry, Faculty of Science, Selçuk University, 42031, Konya, Turkey. E-mail: benizgunduz@gmail.com

Alzheimer's disease (Ward, Zhang, and Crichton 2001); the hypothesis advanced indicated that aluminum might exert its toxic effect by using mechanisms which control iron homeostasis, e.g., using transport proteins such as transferrin or interfering with iron homeostasis at the level of iron regulatory proteins.

Aluminium accumulation may increase the risks of neurological and bone diseases, e.g., Alzheimer's disease, Parkinson's disease, encephalopathy, and osteomalacia (Sinczuk-Walczak et al. 2005; Cassidy 2003; Hegde 2004). These pathologies occurred most commonly in chronic renal failure patients maintained on regular hemodialysis and in patients receiving long-term parenteral nutrition. Furthermore, in workers occupationally exposed to Al-containing dusts and fumes, some effects of aluminum on the nervous system functions were observed, manifested mostly by neurobehavioral disorders, cognitive impairment, and changes in the brain's bioelectric functions (Crappier, Krishnan, and Dalton 1973). Therefore, the evaluation of aluminum levels in biological fluids for prevention of aluminum overload has attracted considerable attention in the field of clinical chemistry. Several instrumental techniques have been employed for this purpose such as Electro Thermal Atomic Absorption Spectroscopy (ETAAS), Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS), Neutron Activation Analysis (NAA), High-Performance Liquid Chromatography (HPLC), and fluorimetry (Magalhaes et al. 2002; Wahlen et al. 2005; Sharif et al. 2004; Lian et al. 2003; Saito et al. 2005; Kashimura et al. 2003; Tamada 2004; Suzuki, Imai, and Kamiki 1989; Guray et al. 2005; Zajun et al. 2007). Although ETAAS and ICP-MS techniques are generally preferred because of their excellent sensitivity and specificity, their rather costly maintenance limit the usage of these instruments.

Schiff bases and their metal complexes are becoming increasingly important as biochemical, analytical, industrial, and antimicrobial agents (Johnson et al. 1982; Temel, Taşkın, and Şekerci 2004). Schiff bases play an important role as central ligands in main group and transition metal coordination chemistry (Bulut et al. 2005; Thakkar and Patil 2000; Bermejo et al. 1999; Temel, Çakır, Otludil 2001; Temel, Çakır, and Uğraş 2001; Temel, İlhan, and Şekerci 2002). Metal complexes of tetradentate Schiff base ligands find applications as models of certain metal enzymes and in catalysis and materials chemistry (Garoufis et al. 1998). Schiff base complexes are known to have antifungal activity, which is increased by the presence of a hydroxy group in the ligand (Lin 1993). Fluorimetric methods are generally sensitive as an analytical technique for aluminum(III) determination at trace levels. Several methods have been described for the fluorimetric determination of aluminum based on the formation of metal complexes (Chisari et al. 1984; Abid and Fenton 1985; Elkins and Nelson 2001; Tabrizi 2007; Albendín et al. 2003; Buratti et al. 2006; Brach-Papa et al. 2002; Takeuchi et al. 2001; Zhang, Xu, and Ren 2000). In a previous paper (Gündüz et al. 2005), we described a spectrofluorimetric method for the determination of trace amounts of aluminum(III) in diluted hemodialysis solution by using N,N-disalicylidene-1,3-diamino-2-hydroxypropane (DSAHP). However, in this study, a new synthesized Schiff base was used to form an aluminum complex. For this reason, we aimed to investigate the fluorescence properties of aluminum(III) complexes of N,N'-bis-(salicylidene)-1,4-diamino buthane (BUTAS), which was formed to complex with aluminum(III). In order to complete the coordination of this complex, 4-methyl-2-aminophenol (OAP) was added, and then the fluorescence properties of complex was studied. The emission spectra of both this Schiff base and its aluminum

complex in *N,N*-dimethylformamide were measured by changing excitation wavelengths. Then the fluorescence intensities of the BUTAS-OAP and Al(III)-BUTAS-OAP complex at the optimum excitation ( $\lambda_{\text{ex}}$ ) and emission wavelengths ( $\lambda_{\text{em}}$ ) were determined in this solvent. Calibration curve was plotted in the optimum conditions and lowest detection limit for aluminum was found.

## EXPERIMENTAL

### Apparatus and Chemicals

A *Shimadzu RF-5000* was used in the study. The spectrofluorometer was calibrated with a 2–10  $\mu\text{g/L}$  solution of uranine (sodium salt of fluorescein). The slit width was fixed at 5 nm for both excitation and emission monochromators. All pH measurements were made with a Orion 720 digital pH-meter with a combined glass-Ag/AgCl electrode.

The Schiff base (BUTAS) used in the experiments was synthesized by Temel, Çakır, Otludil et al. (2001). A stock solution of 1 mM of this Schiff base and OAP were prepared in *N,N*-dimethylformamide (DMF), and these solutions were diluted to suitable concentrations for the working solutions.

The aluminum(III) stock solution, 100 ppm was prepared from the standard 1000 ppm aluminum(*Merck*) that are used for the atomic absorption spectroscopy. The commercial Bikardi-A and Bikardi-B solutions from Farma-Kon Pharmacy Industry (Turkey) were mixed in appropriate amounts for the hemodialysis solution. One liter of Bikardi-A solution contains 214.800 g NaCl, 2.612 g KCl, 7.720 g  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , 3.558 g  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , and 4.207 g  $\text{CH}_3\text{COOH}$  (99–100%) per liter. One liter of Bikardi-B solution contains 84 g  $\text{Na}(\text{HCO}_3)_2$ . The diluted hemodialysis solution was prepared by mixing 1000 ml Bikardi-A and 1225 ml Bikardi-B with 32775 ml of deionized water. The ion concentrations of diluted hemodialysis solution (one liter) were as follows: Na = 140.0 mmol, K = 1.0 mmol, Ca = 1.5 mmol, Mg = 0.5 mmol, Cl = 110.0 mmol,  $\text{CH}_3\text{COO}$  = 2.0 mmol,  $\text{HCO}_3$  = 33.0 mmol, and OsM = 288.0 mmol. All other inorganic salts were purchased from Merck. Ultrapure water was used to prepare the solutions throughout the experimental studies.

### Procedure

Into 25 mL calibrated flasks, appropriate volumes of stock aluminum(III) solutions were put and 2.5 mL of 0.1 mM BUTAS and OAP solutions, 1.5 mL of 20% ammonium acetate solution, and 10.0 mL DMF were added. The pH values of these solutions were adjusted to 5.0 with 1 M HCl or 1 M NaOH. 30 minutes was allowed at 40°C for the formation of the complex and the volumes of the solutions were increased to 25 mL with water. Fluorescence intensities of these solutions were measured at room temperature.

## RESULTS AND DISCUSSION

### Formation of an Aluminum-Schiff Base Complex

According to the general procedure, BUTAS was hydrolyzed in an aqueous solution to liberate salicylaldehyde (SAL), which then reacted with aluminum(III)

and OAP to form a fluorescent Schiff base complex (Fig. 1), (Aoki, Matsunaga, and Watanabe 1989). Such a reaction had previously been utilized for the fluorimetric determination of zinc (Watanabe and Aoki 1986), aluminum (Watanabe and Aoki 1986), and magnesium (Watanabe and Aoki 1986). Although the same complex is formed when *N*-Salicylidene-*o*-aminophenol (SOAP) is used instead of BUTAS and OAP, the procedure in this study has the advantage that the most suitable concentrations of SAL and OAP can be selected to obtain the optimum fluorescence conditions and, therefore, fluorescence intensity of the reagent blank can be decreased.

### Excitation and Emission Spectra

The excitation and emission spectra of the systems investigated are shown in Fig. 2. The results indicated that on adding 1.35 ppb Al(III), the fluorescence intensity of the Al(III)-BUTAS-OAP complex increased about two times compared with the system without Al(III). The maximum excitation wavelength was at 410 nm, and the emission at 526 nm was most intense. The excitation and emission wavelengths for the blank solution which has BUTAS-OAP and solvent medium were found to be 410 and 526 nm, respectively. As a result, Al(III) increased the fluorescence intensity of BUTAS-OAP.

### Effect of Solvent Medium

The solvent medium had a great effect on the fluorescence intensity of the Al(III)-BUTAS-OAP complex. In order to determine the solvent medium, the concentration ratios of DMF and water were investigated by changing the percentage of DMF between 20–80%. The fluorescence intensity of the Al(III)-BUTAS-OAP complex changed with a decrease or increase in the amount of DMF solution. The fluorescence intensity of the complex system was decreased due to solubilities of the inorganic reagents in a high percentage of DMF and solubilities of the organic reagents in a low percentage of DMF as well. Therefore, the best solvent medium was chosen as 50% DMF, 50% (v/v) water for aluminum complex.

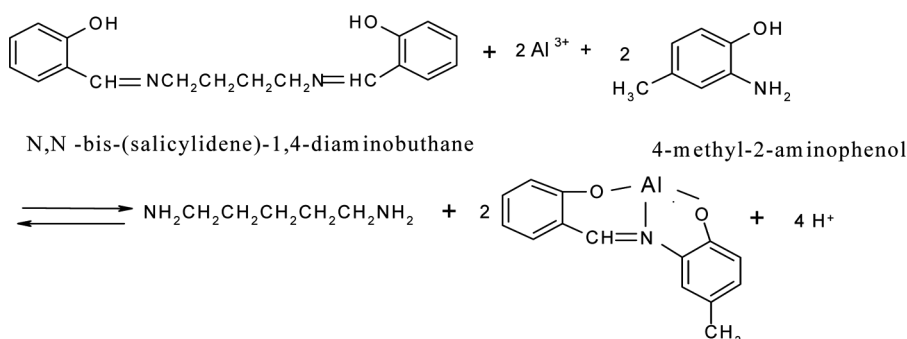
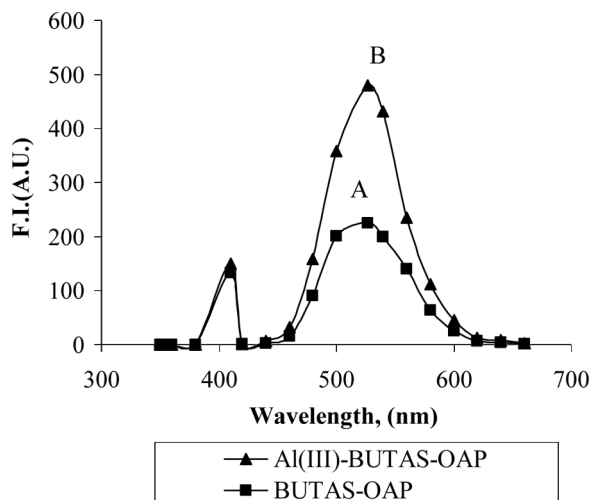


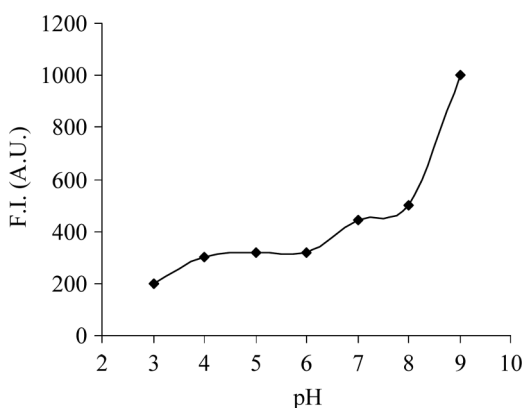
Figure 1. Complex formation reaction.



**Figure 2.** Emission spectra of BUTAS-OAP (A) and Al(III)-BUTAS-OAP complexes (B). [BUTAS]= 0.1 mM, [OAP]=0.1 mM,  $[Al^{3+}] = 1.35$  ppb, pH = 5.0, 50% DMF- 50% water medium.

### Effect of pH

A series of the Al(III)-BUTAS-OAP complex solutions at pH intervals between 2 and 9 containing same concentrations of aluminum(III) were prepared and fluorescence intensities were measured at optimum wavelengths. The fluorescence intensities were plotted against the pH (Fig. 3). The optimum pH interval for the formation of the complex was 5.0. We did not prefer pH 6 and 7, because aluminum hydroxide began to precipitate at these pH intervals. Since a series of different aluminum ionic complex such as  $AlO_2^-$  were formed, fluorescence intensity of this complex system was suddenly increased above pH 8.



**Figure 3.** The effect of pH on the fluorescence intensity of Al(III)-BUTAS-OAP complex. [BUTAS]=0.1 mM, [OAP]=0.1 mM,  $[Al^{3+}] = 0.67$  ppb, 50% DMF- 50% water medium,  $\lambda_{ex} = 410$  nm and  $\lambda_{em} = 526$  nm.

### Effect of Ligand Concentration (BUTAS-OAP)

In order to determine optimum ligand concentration, the concentration of BUTAS-OAP in its transition complex should be carefully monitored because BUTAS-OAP is a very fluorescent reagent. For this reason, a series of Al(III)-BUTAS-OAP complex solutions were prepared by using 0.01, 0.1, and 1 mM of BUTAS-OAP solutions and by aluminum solution of 1.35 ppb. Under optimal conditions, fluorescence intensities were measured in order to determine the effect of BUTAS-OAP concentration on fluorescence intensities of the complexes. The optimal BUTAS-OAP concentration was found to be 0.1 mM, in which the fluorescence intensity was maximum (Fig. 4).

### Effect of Temperature on Complex Formation Time

The effect of temperature on the fluorescence measurements was studied by heating the cell thermostatically between 10–80°C. The fluorescence intensity was increased up to 40°C and decreased gradually thereafter. Therefore, a temperature of 40°C was used throughout the experiments.

Formation of the complex and fluorescence intensity depends significantly on temperature. In high temperature, complex fluorescence was quenched slightly owing to self-absorption of the reagent. As a result, fluorescence intensity was maximum in low temperatures. When the maximum fluorescence intensity of the complex was reached, it could remain at this state at least 30 min at 40°C.

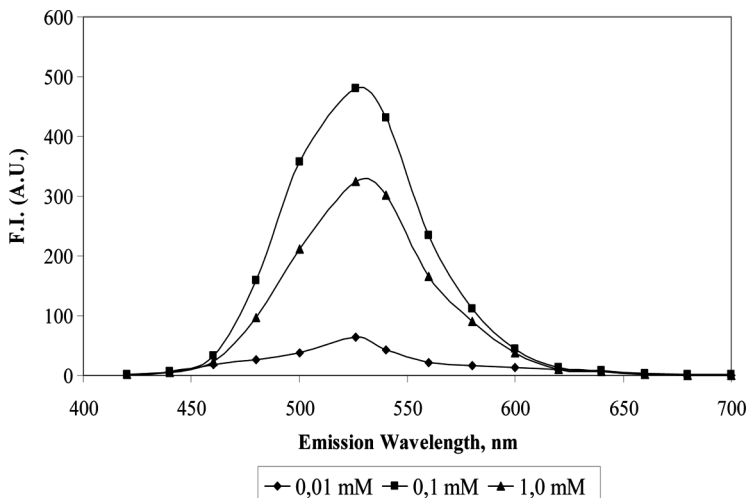
### Stoichiometry of the Al(III)-BUTAS-OAP Complex

Complex stoichiometry was determined by using the continuous variation method that was adapted to the spectrofluorimetric method. In the optimal experimental conditions, fluorescence intensities of Al(III)-BUTAS-OAP complex solutions, which were prepared according to complex formation reaction given in Fig. 1, were plotted against the volume of the ligand (mole ratio of BUTAS/OAP was 1:2). From this curve BUTAS-OAP: aluminum(III) mole ratio was 6:4, in which the maximum fluorescence intensity was obtained (Fig. 5).

### Effect of Foreign Ions

It is known that Schiff bases form complexes with many metal ions, and aluminum interacts with many anions. The effects of various cations and anions and effects of ions in the hemodialysis solution were investigated in order to find out whether this method could be used to detect aluminum in hemodialysis solutions.

A systematic study of the interference of foreign ions in the determination of Al(III) (1.35 ppb) was carried out. For this study, different ions were first added to give a 1000-fold of (m/m) excess over aluminum. The investigated ions and their tolerance ratios are given in Table 1. Various reactives were tried to rid the influence of  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{F}^-$  ions, which are also given in Table 1. Thiocyanate relieves the effect of cobalt (II), thiosulfate and thiourea relieve the effect of



**Figure 4.** The effect of ligand (BUTAS-OAP) concentration on the fluorescence intensity of Al(III)-BUTAS-OAP complex.  $[Al^{3+}] = 1.35$  ppb, pH = 5.0, 50% DMF- 50% water medium,  $\lambda_{ex} = 410$  nm and  $\lambda_{em} = 526$  nm.

copper(II), *o*-phenanthroline and ascorbate relieves the effect of iron(III), and beryllium sulfate relieves the effect of fluoride (Garcia de Torres et al. 1989).

### Analytical Characteristics

Under the optimum conditions, there are linear relationships between the fluorescence intensity and metal concentration. The calibration graphic was plotted for aluminum(III) under the optimum conditions. The regression equation of calibration curve of aluminum(III) was  $I_f = 1.97C + 2.75$  and the correlation coefficient was 0.9960. With this method, aluminum(III) can be detected within a concentration interval of 0.11–1.62 ppb and the lowest detection limits being 0.07 ppb for aluminum(III).

**Table 1.** Effect of foreign ions on spectrofluorimetric determination of aluminum(III) in diluted hemodialysis solutions

Tolerance limit (mole/mole) <sup>a</sup>	Foreign ions	Masking agent
>1000	$Cl^-$ , $Br^-$ , $CH_3COO^-$ , $NO_3^-$ , $HCO_3^-$ , $K^+$ , $Na^+$ , $Ca^{2+}$ , $Mg^{2+}$ , $Ba^{2+}$ , $Zn^{2+}$ , $Mn^{2+}$	
1000	$Co^{2+}$ , $Cr^{3+}$ , $Ni^{2+}$ , $SO_3^{2-}$ , $I^-$ , $SO_4^{2-}$ , $S_2O_3^{2-}$ , $NO_2^-$ , $CO_3^{2-}$	Thiocyanide (5.00 M) for $Co^{2+}$
100	$H_2PO_4^-$ , $PO_4^{3-}$	
10	$Fe^{2+}$ , $Fe^{3+}$ , $Cd^{2+}$ , $Cu^{2+}$	Thiourea (14.0 M) or thiosulphate (0.75 M) for $Cu^{2+}$ , ascorbate (0.10 M) or <i>o</i> -phenantrolin (0.15 M) for $Fe^{3+}$
1	$F^-$	$BeSO_4 \cdot 4H_2O$ (0.045 $\mu$ M) for $F^-$

<sup>a</sup>Tolerance limits of foreign ions are given as mole ratio of foreign ion to aluminum.



**Table 2.** Spectrofluorimetric determination methods of aluminum(III)

Reagent	$\lambda_{\text{ex,em}}$ (nm)	Solvent	Linear Range (ppb)	Limit of Detection (ppb)	Interferences
8-Hydroxyquinoline <sup>1</sup>	360/415	Chloroform	–	20.00	Ga <sup>3+</sup> , In <sup>3+</sup> , Cu <sup>2+</sup> , Fe <sup>3+</sup> , Co <sup>2+</sup> , Ni <sup>2+</sup> , Bi <sup>3+</sup>
Morin <sup>2</sup>	440/525	Ethanol-Water	–	50.00	Cu <sup>2+</sup> , Cr <sup>3+</sup> , Fe <sup>3+</sup> , F <sup>-</sup> , PO <sub>4</sub> <sup>3-</sup>
OBSH <sup>3</sup>	390/475	DMF-Water	0–200	5.00	Ga <sup>3+</sup> , In <sup>3+</sup> , Zr <sup>4+</sup> , Pd <sup>2+</sup> , C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> , F <sup>-</sup> , EDTA
SHPA <sup>4</sup>	383/440	Ethanol-Water	4–80	4.00	In <sup>3+</sup> , Be <sup>2+</sup> , As <sup>5+</sup> , Zn <sup>2+</sup> , F <sup>-</sup> , EDTA
OSH <sup>5</sup>	387/474	DMF-Water	0–160	5.00	Ga <sup>3+</sup> , In <sup>3+</sup> , Sb <sup>3+</sup> , Zr <sup>4+</sup> , Be <sup>2+</sup> , F <sup>-</sup> , As <sup>5+</sup> , P <sub>2</sub> O <sub>7</sub> <sup>2-</sup>
SABH <sup>6</sup>	375/450	Water	0–140	1.40	Be <sup>2+</sup> , Ba <sup>2+</sup> , Fe <sup>3+</sup> , EDTA, Sc <sup>3+</sup> , Ga <sup>3+</sup> , C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> , Ni <sup>2+</sup>
SAPH <sup>7</sup>	384/468	DMF-Water	1–50	0.42	Ag <sup>+</sup> , Au <sup>3+</sup> , Cd <sup>2+</sup> , Hg <sup>2+</sup> , Zr <sup>4+</sup> , C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> , Striat
5-Br-SASH <sup>8</sup>	370/460	Water	0–120	1.10	Ga <sup>3+</sup> , Be <sup>2+</sup> , Fe <sup>3+</sup> , F <sup>-</sup> , H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>
DSAPH <sup>9</sup>	270/422	Dioxane-Water	0–2.7, 2.7–27, 27–270	0.27	Fe <sup>3+</sup> , Cu <sup>2+</sup> , CrO <sub>4</sub> <sup>2-</sup> , F <sup>-</sup> , C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>
BUTAS-OAP (this study)	410/526	DMF-Water	0.11–1.62	0.07	Fe <sup>2+</sup> , Fe <sup>3+</sup> , Cd <sup>2+</sup> , Cu <sup>2+</sup>

<sup>1</sup>Rees, 1962; <sup>2</sup>Will, 1961; <sup>3</sup>Gomez Ariza, 1984; <sup>4</sup>Gallego, 1983; <sup>5</sup>De Pablos, 1986; <sup>6</sup>Cui, 1992; <sup>7</sup>Manuel-Vez, 1994; <sup>8</sup>Jiang, 1997; <sup>9</sup>Gündüz, 2005.

In the literature, various reagents such as bN,N'-oxalylbis(salicylaldehyde hydrazone) (OBSH), pyridine-2-aldehyde salicyloylhydrazone (SHPA), N-oxalylamine salicylaldehyde hydrazone (OSH), salicylaldehyde benzoylhydrazone (SABH), salicylaldehyde picolinoylhydrazone (SAPH), and N,N'-disalicylidene-1,3-diamino-2-hydroxy propane (DSAHP) were proposed for the determination of aluminum(III) by using the spectrofluorimetric method. The excitation and emission wavelength, solvent media, linear range, limit of detection, and interferences of these methods are given in Table 2. Table 2 illustrates that the limit of detection of the proposed method in this study, which was based on using the BUTAS-OAP ligand combination, and it was lower than those in the other methods.

In addition, the number of interferent (foreign) ions is less than in other methods and can be masked to a great extent. This also indicates that detection of aluminum using the fluorescence properties of Al(III)-BUTAS-OAP complex may be superior to other methods in detecting aluminum.

### Determination of Aluminum in Hemodialysis Solutions

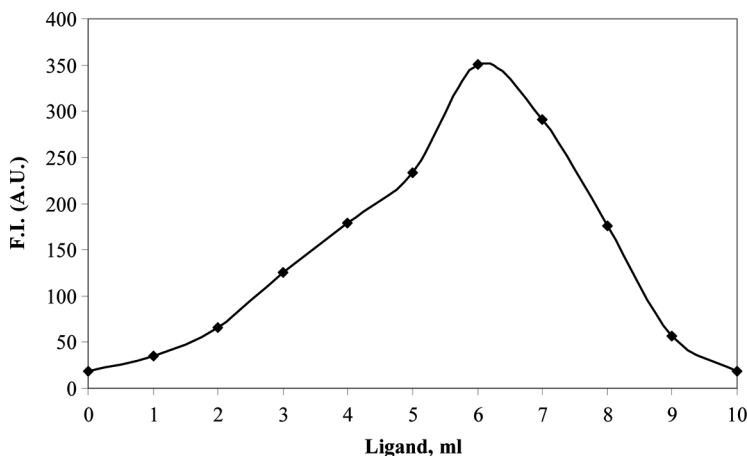
The foreign ions generally have considerable effect on the fluorescence intensity due to complex formation. For this reason, the effects of foreign ions and the ions in the hemodialysis solutions that are likely to affect aluminum(III) determination were studied. The ions which have effects on the proposed method are given in Table 1. Because of the possible minute matrix effects of the proposed method in the determination of aluminum(III) in diluted hemodialysis solutions, determination of aluminum(III) with the standard addition method was preferred. The regression equation of the calibration curve of aluminum(III) by the standard addition method was  $I_f = 340.9C + 19.7$ , and the correlation coefficient,  $r^2$ , was 0.9988. Aluminum (III) was detected in five chosen hemodialysis solutions and the results are tabulated in Table 3. In order to control the validity of the method for determination of aluminum(III) in diluted hemodialysis solutions, aluminum(III) was detected in the same solutions using the method described in British Pharmacopoeia. The results obtained from these experiments are also tabulated in Table 3. The results of the method described in British Pharmacopoeia and the results of this developed method for the detection of aluminum(III) in diluted hemodialysis solutions are in correlation with each other within 95% confidence limits.

For the statistical comparison of the accuracy of the proposed method with the accepted standard and routinely used method described in the British

**Table 3.** Determination of aluminum(III) in hemodialysis solution

	British pharmacopoeia method	The proposed schiff base method
Mean values of aluminum (ppb)	$0.072 \pm 0.010^a$	$0.081 \pm 0.0009^a$
Number of experiments ( <i>N</i> )	5	5
Standard deviation ( <i>s</i> )	0.008	0.007
Relative Standard deviation ( <i>s</i> )	11.111	8.641
Variance ( <i>s</i> ) <sup>2</sup>	$6.4 \times 10^{-6}$	$4.9 \times 10^{-6}$
Reproducibility ( <i>r</i> )	0.315	0.272

<sup>a</sup>Confidence interval is in the dependence level of 95%.



**Figure 5.** Determination of stoichiometry of Al(III)-BUTAS-OAP complex by using the continuous variations methods. Reaction conditions: pH=5.0, 50% DMF- 50% water medium,  $\lambda_{\text{ex}} = 410 \text{ nm}$  and  $\lambda_{\text{em}} = 526 \text{ nm}$ .

Pharmacopoeia, the  $F$  test was used. Since within 95% confidence limit  $F_{\text{exp}}$  (1.31)  $< F_{\text{table}}$  (5.63), there is no difference between the accuracy of these two methods.

## CONCLUSION

This proposed method is based upon the increasing effect of aluminum(III) on the fluorescence intensity of the BUTAS-OAP. Furthermore, new synthesized ligand (BUTAS) was used for the formation of the Al(III)-BUTAS-OAP complex. In this method, fluorescence intensity of the fluorescent ligand (BUTAS-OAP) is increased by the addition of aluminum(III) solution. Thus, aluminum(III) is determined quantitatively, and, as a result, the proposed method can be used with good accuracy and precision for the determination of trace aluminum(III).

## REFERENCES

- Abid, K. K., and D. E. Fenton. 1985. Lanthanide complexes of compartmental ligands. *Inorg. Chim. Acta* 109: L5-L7.
- Albendín, G., M. P. Manuel-Vez, C. Moreno, and M. García-Vargas. 2003. Reverse flow-injection manifold for spectrofluorimetric determination of aluminum in drinking water. *Talanta* 60: 425-431.
- Aoki, I., T. Matsunaga, and K. Watanabe. 1989. Substituent-group effects on the fluorescence of aluminum-Schiff base complexes and their application to the determination of aluminum. *Bull. Chem. Soc. Jpn.* 62: 2369-2374.
- Bermejo, M. R., A. Sousa, A. Garcia-Deibe, M. Manerio, M. Sanmartin, and J. Fondo. 1999. Synthesis and characterization of new manganese(III) complexes with asymmetrical ONSN Schiff bases. *Polyhedron* 18: 511-518.
- Brach-Papa, C., B. Coulomb, J. -L. Boudenne, V. Cerda, and F. Theraulaz. 2002. Spectrofluorimetric determination of aluminum in drinking waters by sequential injection analysis. *Anal. Chim. Acta* 457: 311-318.

- British Pharmacopoeia. 2006. Haemodialysis solutions, water for diluting concentrated. 2637.
- British Pharmacopoeia. 2006. Haemodialysis solutions. 2634.
- Bulut, H., M. Karatepe, H. Temel, M. Şekerci, and M. Koparir. 2005. Studies on the antiviral and cytotoxic activity of Schiff bases derived from 1,2-bis-(o- and p-aminophenoxy) ethane and salicylaldehyde. *Asian J. Chem.* 17: 2793–2796.
- Buratti, M., M. Valla, O. Pellegrino, F. M. Rubino, and A. Colombi. 2006. Aluminum determination in biological fluids and dialysis concentrates via chelation with 8-hydroxyquinoline and solvent extraction/fluorimetry. *Anal. Biochem.* 353: 63–68.
- Cassidy, M. J. D. 2003. Renal osteodystrophy. *Med.* 31: 56–61.
- Chisari, A., A. Musumeci, M. Vidali, and A. Seminara. 1984. Lanthanide(III) complexes with a Schiff-base as a binucleating ligand. *Inorg. Chim. Acta* 81: L19–L21.
- Crapper, D. R., S. S. Krishnan, and A. J. Dalton. 1973. Brain aluminum distribution in Alzheimer's disease and experimental neurofibrillary degeneration. *Science* 180: 511–513.
- Croom, J., and I. L. Taylor. 2001. Neuropeptide Y, peptide YY and aluminum in Alzheimer's disease: Is there an etiological relationship? *J. Inorg. Biochem.* 87: 51–56.
- Cui, W. C., B. Tang, and H. M. Shi. 1992. Spectrofluorimetric and spectrophotometric determination of aluminium with the salicylaldehyde benzoylhydrazone. *Fenxi Huaxue* 20(1): 11.
- De Pablos, F., J. L. Gomez Ariza, and F. Pino. 1986. N-oxalylamine(salicylaldehyde hydrazone) as an analytical fluorimetric reagent for the determination of nanogram amounts of aluminium. *Analyst* 111: 1159–1162.
- Elkins, K. M., and D. J. Nelson. 2001. Fluorescence and FT-IR spectroscopic studies of Suwannee river fulvic acid complexation with aluminum, terbium and calcium. *J. Inorg. Biochem.* 87: 81–96.
- Gallego, M., M. Valcarcel, and M. Garcia-Vargas. 1983. Spectrofluorimetric and spectrophotometric determination of aluminium with the salicyloylhydrazones of pyridine-2-aldehyde and pyridoxal. *Analyst* 108: 92–98.
- Garoufis, A., S. Kasseoluri, C. A. Mitsopoulou, J. Sletten, C. Papadimitriou, and N. Hadjiliadis. 1998. Metal complexes of the Schiff base ligand L=1,2-bis(2'-pyridylmethyleneimino)benzene with Ni<sup>2+</sup>, Fe<sup>2+</sup> and Cu<sup>2+</sup> and their reactions with bridged bidentate ligands. The crystal structure of the complex [NiL(H<sub>2</sub>O)<sub>2</sub>]Cl<sub>2</sub>. *Polyhedron* 18: 39–47.
- Garcia de Torres, A. G. D., C. B. Ojeda, F. S. Rojas, M. E. U. Pozo, and C. Pavon. 1989. Selective fluorimetric determination of aluminium with 1,5-bis(salicyl methylene-amino) carbonylhydrazide and 1,5-bis(salicyl methyleneamino) guanidine. A comparative study. *Analyst* 17: 592–595.
- Gomez Ariza, J. L., M. L. Margues, and M. T. Montana. 1984. N,N'-oxalylbis(salicylaldehyde hydrazone) as an analytical spectrophotometric and fluorimetric reagent, Part I, Study of the metal reactivity and application to the determination of aluminium. *Analyst* 109: 885–889.
- Gündüz, S. B., S. Küçükolbaşı, O. Atakol, and E. Kılıç. 2005. Spectrofluorimetric determination of trace aluminum in diluted hemodialysis solutions. *Spectrochim. Acta A* 61: 913–921.
- Guray, T., Ü. D. Uysal, T. Gedikbey, and A. A. Huseyinli. 2005. 2,2',3,4-Tetrahydroxy-3'-sulpho-5'-nitroazobenzene for spectrophotometric determination of aluminium in pharmaceutical suspensions and granite. *Anal. Chim. Acta* 545: 107–112.
- Hegde, M. L., P. Shanmugavelu, B. Vengamma, T. S. S. Rao, R. B. Menon, R. V. Rao, and K. S. J. Rao. 2004. Serum trace element levels and the complexity of inter-element relations in patients with Parkinson's disease. *J. Trace Elem. Med. Biol.* 18: 163–171.
- Jiang, C., B. Tang, R. Wang, and J. Yen. 1997. Spectrofluorimetric determination of trace amounts of aluminum with 5-bromo-salicylaldehyde salicylhydrazone. *Talanta* 44: 197–202.
- Johnson, D. K., T. B. Murphy, N. J. Rose, and W. H. Goodwin. 1982. Cyto-toxic chelators and chelates .1. inhibition of DNA-synthesis in cultured rodent and human-cells by

- aroylhydrazones and by a copper(II) complex of salicylaldehyde benzoyl hydrazone. *Inorg. Chim. Acta* 67: 159–165.
- Kashimura, K., Y. Mizushima, E. Hoshino, and S. Matsubara. 2003. Kinetic differentiation mode chromatography using 8-quinolinol and fluorimetric detection for sensitive determination of aluminum adhering to the gastric mucosa. *J. Chromatogr. B* 791: 13–19.
- Lian, H., Y. Kang, A. Yasin, S. Bi, D. Shao, Y. Chen, L. Dai, and L. Tia. 2003. Determination of aluminum in environmental and biological samples by reversed-phase high-performance liquid chromatography via precolumn complexation with morin. *J. Chromatogr. A* 993: 179–185.
- Lin, C. H. 1993. Synthesis and characterization of some indium (III) complexes of Schiff-bases. *Synth. React. Inorg. Met.-Org. Chem.* 23: 1097–1106.
- Magalhaes, C. G., K. L. A. Lelis, C. A. Rocha, and J. B. Borba da Silva. 2002. Direct determination of aluminum in serum and urine by electrothermal atomic absorption spectrometry using ruthenium as permanent modifier. *Anal. Chim. Acta* 464: 323–330.
- Manuel-Vez, M. P., and M. Garcia-Vargas. 1994. The synthesis, characterization and application of SAPH to the determination of aluminum in agricultural soils. *Talanta* 41: 1553–1555.
- Rees, W. T. 1962. Fluorimetric determination of very small amounts of aluminum. *Anal. Chim. Acta* 87: 202–206.
- Saito, S., T. Anada, S. Hoshi, and K. Akatsuka. 2005. Chemical suppression of contaminant metal ions using a metastable state in precolumn derivatizing HPLC: An ultratrace fluorometric detection of Al(III). *Anal. Chem.* 77: 5332–5338.
- Sharif, A. A. M., H. Ghafourian, A. Ahmadiniar, S. Waqif Husain, M. Saber-Tehrani, and H. Ghods. 2004. Determination of aluminum levels in serum and red blood cells from long-term hemodialysis patients using instrumental neutron activation analysis. *J. Radioanal. Nucl. Chem.* 262: 473–477.
- Sinczuk-Walczak, H., W. Matczak, G. Razniewska, and M. Szymczak. 2005. Neurological and neurophysiological examinations of workers occupationally exposed to aluminum. *Med. Pract.* 56: 9–17.
- Suzuki, Y., S. Imai, and T. Kamiki. 1989. Fluorometric determination of aluminum in serum. *Analyst* 114: 839–842.
- Tabrizi, A. B. 2007. Cloud point extraction and spectrofluorimetric determination of aluminum and zinc in foodstuffs and water samples. *Food Chem.* 100: 1698–1703.
- Takeuchi, V., S. Inoue, M. Yamamoto, M. Tsuji, and T. Miwa. 2001. Fluorimetric determination of magnesium and aluminum via complexation with oxine in high-performance liquid chromatography. *J. Chromatogr. A* 910: 373–376.
- Tamada, T. 2004. Fluorometric determination of aluminum in human serum and whole blood. *Bunseki Kagaku* 53: 435–440.
- Temel, H., Ü. Çakır, B. Otludil, and H. İ. Uğraş. 2001. Synthesis, spectral and biological studies of Mn(II), Ni(II), Cu(II), and Zn(II) complexes with a tetradentate schiff base ligand. complexation studies and the determination of stability constants (Ke). *Synth. React. Inorg. Met.-Org. Chem.* 31: 1323–1337.
- Temel, H., Ü. Çakır, and H. İ. Uğraş. 2001. Synthesis and characterization of Zn(II), Cu(II), and Ni(II) complexes with bidentate Schiff base ligands: Complexation studies and the determination of stability constant (Ke). *Rus. J. Inorg. Chem.* 46: 1846–1850.
- Temel, H., S. İlhan, and M. Şekerci. 2002. Synthesis and characterization of a new bidentate Schiff base and its transition metal complexes. *Synth. React. Inorg. Met.-Org. Chem.* 32: 1625–1634.
- Temel, H., T. Taşkın, and T. Şekerci. 2004. Spectral and antifungal studies of transition metal complexes of N,N'-ethylenebis(salicylideneimine). *Russ. J. Inorg. Chem.* 49: 347–351.

- Thakkar, N. V., and R. M. Patil. 2000. Synthesis of mononuclear metal complexes with some tetradentate Schiff base ligands. *Synth. React. Inorg. Met.-Org. Chem.* 30: 1159–1174.
- Wahlen, R., L. Evans, J. Turner, and R. Hearn. 2005. The use of collision/reaction cell ICP-MS for the determination of elements in blood and serum samples. *Spectroscopy* 20: 84–89.
- Ward, V., Y. Zhang, and R. R. Crichton. 2001. Aluminium toxicity and iron homeostasis. *J. Inorg. Biochem.* 87: 9–14.
- Watanabe, K., and I. Aoki. 1986. Complex-formation of zinc-salicylidine aliphatic monoamines and its application to the fluorometric-determination of zinc. *Bunseki Kagaku* 35: 1–6.
- Watanabe, K., and I. Aoki. 1986. Fluorometric-determination of aluminum with bis-salicylidene-ethylenediamine in the presence of amino-acid. *Bunseki Kagaku* 35: 487–493.
- Watanabe, K., and I. Aoki. 1986. Fluorometric-determination of magnesium with bis-salicylidene ethylenediamine in the presence of amines. *Bunseki Kagaku* 35: 795–801.
- Will, F. 1961. Fluorimetric determination of aluminum in the part-per-billion range. *Anal. Chem.* 33(10): 1360–1362.
- Zaijun, L., L. Naping, Z. Xia, and S. Qijun. 2007. Extraction spectrophotometric determination of aluminum in dialysis concentrates with 3,5-ditertbutylsalicylfluorone and ionic liquid 1-butyl-3-trimethylsilylimidazolium hexafluorophosphate. *J. Pharm. Biomed. Anal.* 43: 1609–1614.
- Zhang, J., H. Xu, and J. L. Ren. 2000. Fluorimetric determination of dissolved aluminium in natural waters after liquid–liquid extraction into *n*-hexanol. *Anal. Chim. Acta* 405: 31–42.