Journal of Taibah University for Science 9 (2015) 601–609

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Spectrofluorimetric determination of aluminium in water samples using N-((2-hydroxynaphthalen-1-yl)methylene) acetylhydrazide

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Available online 7 April 2015

Abstract

A sensitive and selective spectrofluorimetric method has been developed for the rapid determination of aluminium. This method is based on the formation of a complex between aluminium and N-((2-hydroxynaphthalen-1-yl)methylene) acetylhydrazide (HNMA). The fluorescence of the complex is monitored at an emission wavelength of 450 nm with excitation at 385 nm. Optimum complex formation occurred in Tris buffer at pH 6.0. Under the optimum conditions, linear calibration curves were obtained from 50 to 800 ppb. The detection limit was 9.2 ppb (ng mL^{-1}). The maximum relative standard deviation of the method for an aluminium standard of 200 ppb was 2.5%. The effects of surfactants and interference from other ions were studied. The method was successfully applied for the determination of aluminium ions in water samples.

Keywords: Aluminium; N-((2-hydroxynaphthalen-1-yl)methylene) acetylhydrazide (HNMA); Complex formation; Spectrofluorimetric determination

1. Introduction

Aluminium is found in a wide variety of chemical forms throughout the environment. The naturally occurring forms of aluminium are usually stable and do not interfere with biological processes. However, at low pH values, the metal is rendered bioavailable to plants and the food chain from naturally occurring rocks and soil [1]. The toxicity of aluminium to humans, plants, aquatic invertebrates and fish is attributed to its ability to substitute for iron and other metals in proteins. Aluminium toxicity has been recognized to be a major factor that limits the growth of plants in acidic soil [2].

Aluminium is a well-known flocculating agent in potable water treatment units, and hence, it is found at parts per billion levels in most drinking water. According to the WHO, the permissible level of aluminium in drinking water is 200 ppb [3].

The clinical biochemistry of aluminium is mostly associated with its neurotoxicity [4]. Aluminium accumulation has been associated with a variety of human pathologies including renal failure, dementia, encephalopathy [5], Alzheimer's disease [6] and Parkinson's disease [7]. Recently, it has been reported that the

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Peer review under responsibility of Taibah University.

Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.jtusci.2015.03.009

toxicity of aluminium may be attributed to its interference with various metabolic processes involving Ca^{2+}, Mg^{2+}, Fe^{2+} and Fe^{3+} [8].

Due to the extensive uses and wide occurrence of aluminium in nature, many methods have been developed for its determination. The most commonly used methods to determine the amount of aluminium are inductively coupled plasma atomic emission spectrometry (ICP-AES) [9], ICP-mass spectrometry (ICP-MS) [10], graphite furnace atomic absorption spectrometry (GF-AAS) [11], and spectrophotometry [12,13]. Spectrofluorimetry, in contrast, is applied more so because of its high selectivity, excellent sensitivity, ease of automation, cost-effectiveness and large linear range of analysis.

Aluminium is not fluorescent in nature, but it can form complexes with fluorogenic ligands [14–28]. The combination of a metal ion and an organic ligand to form a highly fluorescent complex has proven to be a sensitive and specific method for the determination of many metals. Many fluorogenic reagents have been used for the determination of aluminium based on the formation of metal complexes. These include quercetin [14], morin [15,16], purpurin [17], lumogallion [18,19], 8-hydroxyquinoline-5-sulfonic acid [20], oxine [21,22], chromotropic acid [23,24], salicylaldehyde picolinohydrazone [25], *N*,*N*-disalicylidene-1,3-diamino-2-hydroxy propane [26], 8-hydroxy-7-(4-sulfo-1-naphthylazo)-5-quinoline sulfonic acid (HSNQ) [27], N-o-vanillidine-2-amino-p-cresol [28]) and 2-hydroxy-1-naphthylidene-(8-aminoquinoline) [29].

As part of our recent method development [15,16,27,29,30] for the sensitive monitoring of aluminium ions in water, we report herein a novel method for the determination of aluminium using the fluorogenic ligand N-((2-hydroxynaphthalen-1-yl) methylene) acetylhydrazide (HNMA). Factors affecting complexation and the effects of foreign species were studied. Optimum conditions were used for the determination of aluminium in drinking water samples in the presence of other ions. The method was further applied for the determination of aluminium in commercial bottled water, tap water and natural water samples spiked with aluminium. The method was validated by analysing a standard aluminium sample.

2. Experimental

2.1. Apparatus

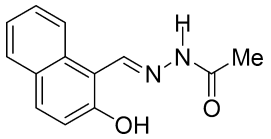
Fluorescence measurements were carried out in a Perkin-Elmer LS55 luminescence spectrometer equipped with a xenon lamp. Instrumental parameters were controlled with FL Winlab Software. The pH was measured on a WTW (3015 Jenway) pH metre calibrated daily with fresh buffer solutions at pH 4, 7 and 9. Absorption spectra were recorded on a Varian-Cary 50 UV–visible spectrophotometer using a 1-cm quartz cell. Infrared spectra were recorded as KBr pellets on a BX Perkin Elmer FT-IR spectrometer in the range of 4000–400 cm^{-1}. Electrospray (ES) mass spectra were recorded on a VG Autospec magnetic sector instrument. Proton nuclear magnetic resonance (^1H NMR) spectra were recorded using a 400 MHz AVANCE Bruker NMR spectrometer. Chemical shifts (δ_{ppm}) were recorded in parts per million (ppm) downfield from TMS (assigned as zero ppm). Elemental analysis for carbon, hydrogen and nitrogen was performed using a Perkin Elmer 2400 CHNS/O Series II Elemental Analyser.

2.2. Reagents and solvents

Aluminium chloride was purchased from Fluka (Buchs, Switzerland). Acetic acid and sodium chloride were purchased from ACROS (USA). Methanol, ethanol and acetonitrile were provided by Sigma–Aldrich (Germany). Sodium acetate, tris(hydroxymethyl) methylamine, magnesium sulfate, iron(III) chloride tetrahydrate, potassium dihydrogen phosphate, sodium bicarbonate, sodium citrate and copper(II) chloride dehydrate were all purchased from BDH Chemicals Ltd. (Poole, England). Calcium nitrate tetrahydrate and potassium chloride were purchased from Qualinges Fine Chemicals (India). An aluminium standard solution (1000 ppm, $\mu g\,mL^{-1}$), traceable to SRM from NIST $Al(NO_3)_3$ in HNO_3, was purchased from Merck-Millipore Chemicals (Germany). All reagents used were of analytical grade, and highly pure water was produced by a Millipore Milli-Q system.

2.3. Synthesis of HNMA

A solution of acetic hydrazide (0.65 g; 10 mmol) in 40 mL of EtOH was added dropwise to a solution of 2-hydroxy-1-naphthaldehyde (1.5 g; 10 mmol) in 25 mL of EtOH and refluxed at 70 °C for 4 h until a yellow precipitate was formed. The precipitate was filtered off and dried. Yield: 1.8 g (79%). ES-MS: $m/z = 227.1$ [M^+]. IR (KBr, cm^{-1}) 3350, 3042, 3100, 1632, 1400–1600. ^1H NMR ($CDCL_3$): 11.71 (1H, s, OH), 11.12 (1H, s, NH), 9.15 (1H, s, CH), 8.20 (1H, d, naph H^{10}), 7.87 (1H, d, naph H^4), 7.74 (1H, t, naph H^6), 7.58 (1H, t, naph H^7), 7.40 (1H, t, naph H^5), 7.21 (1H, d, naph H^9) and 2.02 (3H, s, Me). $C_{13}H_{12}N_2O_2$ (228.25): calcd. C 68.4, H 5.3, N 12.3; found C 68.5, H 5.3, N 12.2.



Scheme 1. Structure of HNAM.

HNMA (Scheme 1) was further used as a reagent for the analysis of aluminium. A stock solution of HNMA (1×10^{-3} M) was prepared by dissolving 5.7 mg of the ligand in a 25.00-mL volumetric flask with methanol. The working solutions were prepared daily by the appropriate dilutions of the stock solution.

2.4. Synthesis of Al-HNMA

The Al^{3+} complexes were prepared by combining different molar quantities of HNMA and $AlCl_3$ in MeOH. To a solution of HNMA (0.20 g; 0.88 mmol) in MeOH (15 mL), a solution of $AlCl_3$ (0.059 g; 0.44 mmol) dissolved in MeOH (5 mL) was added dropwise at room temperature. The yellowish solution formed was left so the solvent would slowly evaporate off. A pale yellow product was formed within a few days. The complexes are air and moisture stable solids, and their characterization data were as follows:

[Al(HNMA)$_2$]Cl: Yield 86%. ES-MS: *m/z* 481.03. IR (KBr, cm^{-1}) 1623. $AlC_{26}H_{22}N_4O_4Cl$: calcd. C 60.41, H 4.29, N 10.84; found C 60.48, H 4.34, N 10.80.
[Al(HNMA)$_3$]: Yield 67%. ES-MS: *m/z* 707.32. IR (KBr, cm^{-1}) 1616.
[Al$_2$(HNMA)$_3$]Cl$_3$: Yield 64%. ES-MS: *m/z* 733.13. IR (KBr, cm^{-1}) 1625.
[Al$_3$(HNMA)]Cl$_8$: Yield 86%. ES-MS: *m/z* 481.03. IR (KBr, cm^{-1}) 1623.

2.5. Preparation of the aluminium chloride standard solution

A stock solution of $AlCl_3$ (1×10^{-3} M) was prepared by dissolving 3.3 mg of $AlCl_3$ in a 25.00-mL volumetric flask with methanol or deionized water in an aqueous system. Working solutions were prepared daily by the appropriate dilutions of the stock solution.

2.6. Preparation of the surfactant solutions

Stock solutions of various surfactants were prepared by dissolving 1.00 g of each surfactant in 100.0 mL deionized water in a volumetric flask. The surfactants include Tween-20, Tween-80, sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB), Triton X-100, sodium dodecyl benzene sulfonate (SDBS) and XH.

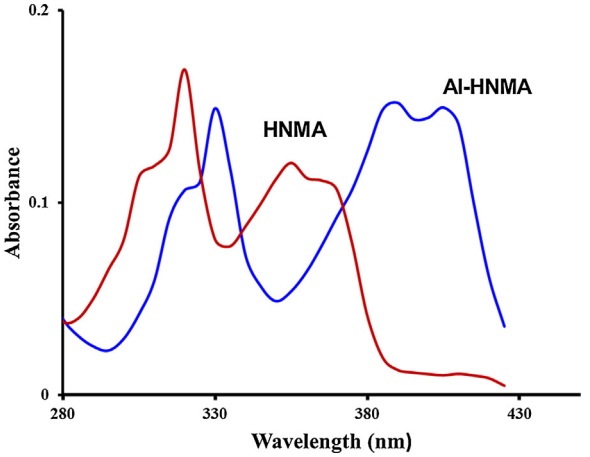


Fig. 1. Absorption spectra of HNAM and its aluminium complex in methanol. [HNAM] = [Al (III)] = 1.0×10^{-6} M.

2.7. Preparation of the water samples

Three different types of water samples, including tap water from the Sultan Qaboos University campus, bottled water and well water, were collected in clean amber bottles. The water samples were filtered with Whatman filter paper to remove standard particulate matter and spiked with appropriate volumes of a 10 ppm standard Al^{3+} solution.

3. Results and discussion

3.1. Spectral characteristics

The electronic absorption spectrum of HNMA in methanol exhibited absorption bands at 320, 355 and 370 nm. When reacted with aluminium ions, a bathochromic shift was observed in all of the absorption bands from 320 to 330 nm, from 355 to 385 nm and from 370 to 405 nm accompanied by a slight decrease in the absorbance of the first peak and an increase in the absorbance of the second and third peaks (Fig. 1). The shifts in the absorption wavelengths indicate that a complex is formed between aluminium and HNMA. Furthermore, the red shifts in the absorption wavelengths upon complexation indicate that the ground state of the ligand is stabilized upon complexation.

The excitation and emission spectra of HNMA and its aluminium complex were investigated in methanol. HNMA exhibited a moderate fluorescence signal at

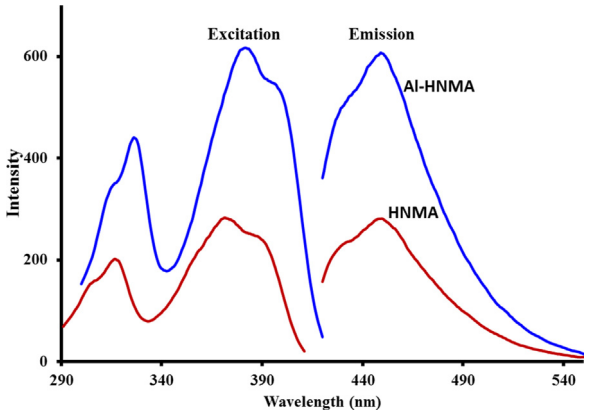


Fig. 2. Excitation and emission spectra of HNAM and its Al complex [HNAM] = 1.0×10^{-6}M, λ_{ex} = 370 nm. λ_{em} = 450 nm.

λ_{em} = 450 nm when exited at 370 nm. Fig. 2 shows the excitation and emission spectra of HNMA and its aluminium complex. Clearly, upon adding aluminium, a bathochromic shift in the excitation wavelength from 370 to 385 nm was observed. Inspection of Fig. 2 indicates that the fluorescence intensity of the Al-HNMA complex increased when compared to that of the ligand alone. This increase in the fluorescence intensity of the complex may be explained as being due to an increase in the rigidity of the complex when compared to the ligand alone. The red shift in the excitation wavelength suggests that the ground state is more stabilized by complexation when compared with the excited state.

3.2. Determination of the stoichiometry of the complex

The ratio of the metal:ligand that will give the maximum signal intensity and hence the maximum complexation of the metal was determined. The fluorescence intensities of various molar ratios of Al(III) to HNMA ranging from 0.1 to 4 were measured. The concentration of HNMA was maintained constant at 1.0×10^{-6} M while the concentration of aluminium was varied from 1.0×10^{-7} to 4.0×10^{-6} M. As observed in Fig. 3, there is a possibility of the formation of more than one complex of aluminium. The fluorescence intensity of the complex increases sharply with an increase in the ratio of aluminium for the lower concentrations up to a molar ratio of two. The fluorescence intensity of the complex remains almost constant for molar ratios between two and three. Upon increasing the molar ratio further to between three and four, a slight increase in the fluorescence intensity was observed. Upon extrapolating the linear parts of the curve, a stoichiometric ratio of approximately two was observed, suggesting that the

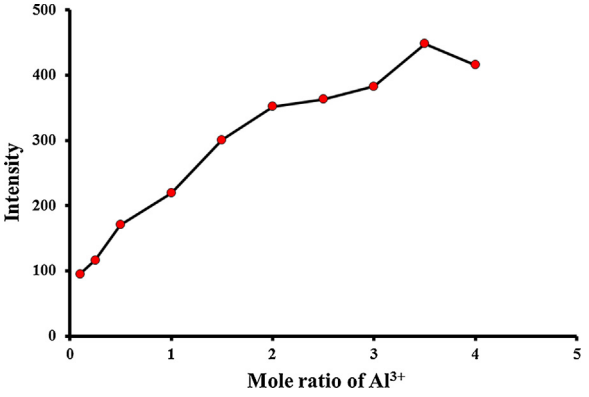


Fig. 3. The fluorescence intensity of Al (NAM) *versus* Al (III) ions ratio. [HNAM] = 1.0×10^{-6} M, [Al (III)] = 1×10^{-7} M to 4×10^{-6} M. λ_{em} = 450 nm, λ_{ex} = 385 nm.

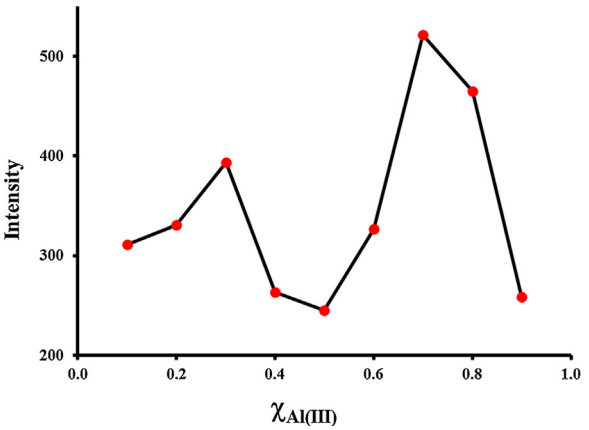


Fig. 4. Determination of the stochiometry of Al(NAM) complex by applying Job's method. λ_{ex} = 385 nm, λ_{em} = 450 nm. [Al (III)] = [HNAM] = 1.0×10^{-6} M.

stoichiometry of one of the complexes was Al_2-NMA, along with the possibility of Al_3-NMA for higher concentrations of aluminium. Similar results were previously reported for the complexation behaviour of Al^{3+} with quercetin [31] and 8-hydroxy-7-(4-sulf-1-naphthylazo)-5-quinoline sulphuric acid (HSNQ) [27]. It was difficult to deduce the complex stoichiometry using the molar ratio method. This is because of the formation of complexes with many different stoichiometries depending upon the concentration of the metal compared to that of the ligand (Section 2.4). The stoichiometry of the complex was further corroborated by a Job's plot. The results presented in Fig. 4 indicate the presence of two complexes. The first complex is observed at a mole fraction of Al:HNMA of 1:3, and the major complex at higher concentrations of aluminium was observed at a mole fraction of 3:1 Al:HNMA. These results support the previous suggestion that

multiple complexes with stoichiometries of $Al(HNMA)_3$ and $Al_3(HNMA)$ may be formed. This is a typical result, as aluminium has been known to form higher charged complexes with morin [32]. Furthermore, it was previously reported that the complexation of aluminium with quinizarin in methanol increases with an increase in the concentration of aluminium due to the formation of supramolecular assemblies [33]. It is reasonable to assume that the complexation of aluminium and HNMA follows a similar behaviour. These results suggest that HNMA can be used for speciation studies of aluminium complexes. The speciation of aluminium with the HNMA ligand was further investigated by ESI-MS in methanol. The spectra were recorded at different molar ratios of Al^{3+} and HNMA under the optimal operational conditions. The ESI-MS spectra indicate the presence of various polynuclear Al^{3+} complexes containing the following species: AlL_2 ($m/z = 481.03$), AlL_3 ($m/z = 707.32$), Al_2L_3 ($m/z = 733.13$) and Al_3L ($m/z = 310.98$), which confirms the speciation of aluminium. It is also noticeable from the spectra that the major species identified in solution with molar ratios of L more than 1 is AlL_2. Interestingly, this species disappears with higher molar ratios of Al (*viz.*, Al:L of 3:1).

3.3. Effect of the Solvent on the complexation

Commonly, solvents affect the fluorescence of molecules through their ability to stabilize ground and excited states differently, thereby changing the probability and the energy of both absorption and emission. The fluorescence behaviour of the complex depends on the solvent because of changes in the relative abilities of the solvents to disrupt and reform intramolecular hydrogen bonding in the molecules in solution in both the ground and excited states. Fig. 5 shows the effects of the solvents on the fluorescence of the Al-HNMA complex. The maximum fluorescence intensity was observed in methanol, followed by butanol, then ethanol, and finally acetonitrile. A slight blue shift in the emission wavelength is observed in ethanol from 450 to 440 nm. The excitation wavelength remained constant at 385 nm for all of the solvents. This behaviour may be explained due to the degree of solubilization of the ligand in different solvents. The relatively higher fluorescence intensity of the complex in methanol may be attributed to the stabilization of the complex due to the hydrogen bonding ability of the solvent. However, the decrease in the fluorescence intensity of the complex in ethanol compared to butanol is rather surprising, and at the moment, no explanation for this phenomenon is available. These results suggest that effects other than a simple hydrogen

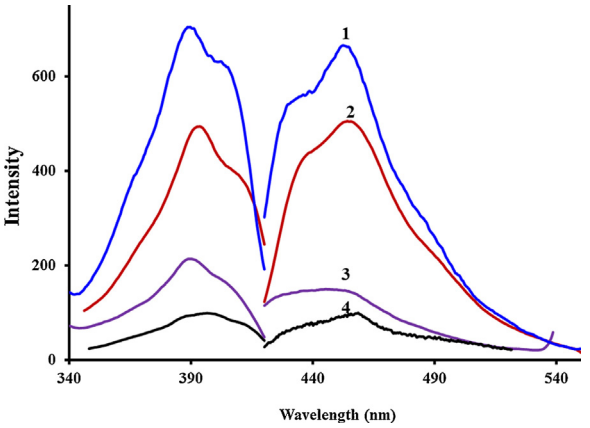


Fig. 5. The effect of solvents on fluorescence intensity of Al (NAM). [HNAM] = [Al (III)] = 1.0×10^{-6}M. (1) Methanol, (2) butanol, (3) ethanol, (4) acetonitrile.

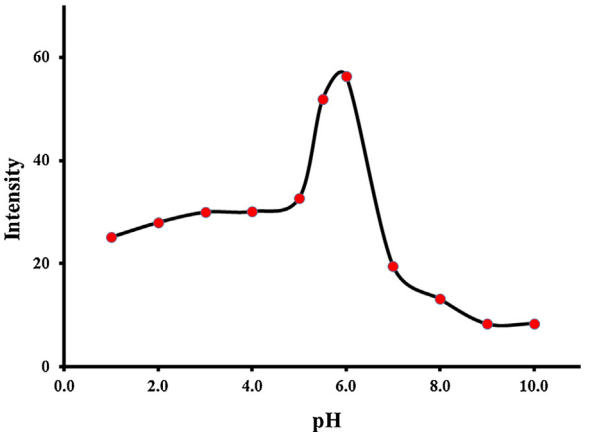


Fig. 6. Influence of pH on fluorescence of Al-NAM. [Al (III)] ions = [HNAM] = 1.0×10^{-6} M, [acetate buffer] = 0.2 M, λ_{ex} = 385 nm. λ_{em} = 450 nm.

bonding model may account for the fluorescence behaviour. The fluorescence intensity of the complex decreased in the aprotic solvent acetonitrile. Similar results were previously reported for the Al-HSNQ complex [27].

3.4. Effect of the pH on the complexation

The pH of the media affects the existing form of the reagent and plays a distinctive role in the metal-chelate formation. Therefore, the pH of the system that will give the maximum complex formation was studied by measuring the fluorescence intensity of Al-HNMA in acetate buffers with different pH values adjusted using dilute hydrochloric acid solutions for the low pH range and dilute sodium hydroxide solutions for the high pH range. The results (Fig. 6) show that the fluorescence intensity

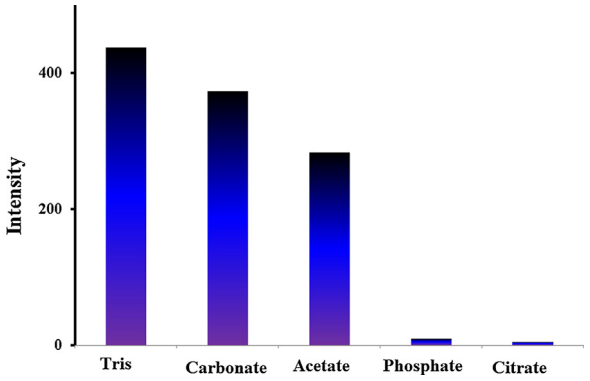


Fig. 7. The effect of varying the type of buffer on fluorescence intensity of Al-NMA complex. [Al (III)] = [HNAM] = 1.0×10^{-6} M. λ_{ex} = 385 nm. λ_{em} = 450 nm.

of the complex increased with an increase in the pH and reached a maximum at a pH of 6.0. A sharp decrease in the fluorescence intensity was observed upon increasing the pH further above 6.0. Thus, a pH of 6.0 was selected as the optimum pH for this study. This behaviour may be explained to be due to the existence of the ligand predominately in the protonated form at low pH values, while at higher pH values, the concentration of OH^- increases, and hence, it competes with HNMA for Al ions, resulting in less Al-HNMA complex being formed. Similar results were previously reported by Al-Kindy et al. [29] for the complex formed between Al and 2-hydroxy-1-naphthylidene-(8-aminoquinoline) where an optimum pH of 5.5 was reported.

3.5. Effect of the type of buffer on the complexation

The effect of the type of buffer on the complex formation of the Al-HNMA system was studied by measuring the fluorescence intensity of various buffers while the pH of the buffer was kept constant at pH 6.0. The maximum complex formation was obtained in the presence of Tris buffer (Fig. 7). Conversely, a lower fluorescence intensity was observed in the presence of citrate and phosphate buffers. These results indicate that citrate and phosphate ions may compete with HNMA for complex formation with Al(III) ions, and hence, less Al-HNMA complex is formed. Tris and carbonate ions, in contrast, experience less complexation with aluminium ions, and hence, higher complexations of aluminium ions with the HNMA ligand are obtained using these ions as buffers.

3.6. Effect of the surfactant

Different surfactants were used to enhance the fluorescence intensity of Al-HNMA. It was observed that all of the surfactants enhanced the fluorescence intensity of the ligand alone when compared to the complex. Those enhancements can be explained to be due to a greater solubilization of the ligand in the presence of surfactants compared to the complex. Maximum enhancement was observed in Tween 20, followed by Triton X-100, XH, and finally Tween 80. These results indicate that favourable solubilization is brought upon by non-ionic surfactants, followed by anionic surfactants and then by cationic surfactants. Because fluorescence enhancement was induced in the presence of the ligand alone, the analytical application was carried out without the addition of surfactant.

3.7. Effect of the time on the complexation

The experimental results show that the fluorescence intensity of the Al-HNMA complex increases with time, reaching a maximum at 20 min, after which the intensity remains constant for 40 min. Therefore, the fluorescence intensity of the complex for this study was measured after a constant time interval of 20 min. Because the complexation of aluminium with HNMA is a slow reaction, a high luminescence signal and hence better detection limit could be obtained by allowing the reaction go to completion. Therefore, in this method, case sensitivity was traded for time.

3.8. Analytical features

Under the optimum experimental conditions, a linear relationship between the fluorescence intensity and aluminium concentration in the range of 50–800 ppb was obtained. The calibration equation was $I = 460.0C - 32.74$ with a correlation coefficient (R^2) of 0.9985 ($n = 5$). The reproducibility of the method was checked by measuring a 200 ppb aluminium standard five times, and relative standard deviation values of 2.5% were obtained. The detection limit according to

Table 1
Effect of interfering species on the recovery of Al (III). $[Al^{3+}]$ = 0.5 ppm [HNMA] = 1×10^{-5} M. λ_{em} = 450 nm, λ_{ex} = 385 nm. Slit width = 3.

Ions	Concentration (ppm)	Recovery (%)
Na^+	100	98.3 ± 1.5
K^+	120	94.6 ± 1.3
Ca^{2+}	60	99.6 ± 1.1
Mg^{2+}	200	81.3 ± 1.3
Cu^{2+}	30	8.0 ± 2.1
Fe^{3+}	100	3.7 ± 2.2

Table 2
Determination of aluminium in water samples. [HNMA] = 1×10^{-5} M. λ_{em} = 450 nm, λ_{ex} = 385 nm. Slit width = 4.

Water sample	Concentration of Al^{3+} added	Concentration of Al^{3+} found	Recovery (%)
Masafi	0.300	0.295	98.3 ± 2.5
Water	0.50	0.470	94.0 ± 2.3
Well	0.30	0.259	86.3 ± 2.1
water	0.50	0.420	86.0 ± 1.9
Tap	0.30	0.279	93.0 ± 1.9
water	0.50	0.450	90.0 ± 1.7

the signal-to-noise ratio of $3S_b/m$, where S_b is the signal of the blank ($n = 5$) and m is the slope, is 9.2 ppb. The quantification limit according to the signal-to-noise ratio of $10S_b/m$, where S_b is the signal of the blank ($n = 5$) and m is the slope, is 31.0 ppb. The figures of merit of the proposed procedure compared favourably with those previously reported in the literature for the determination of Al^{3+} using lumogallion (10 ppb) [19], morin (27 ppb) [34], HSNQ (4 ppb) [27], oxine (5.1 ppb) [35] and chromotropic acid (100 ppb) [36] but was inferior to the figures of merit obtained using N,N-disalicylidene-1,3-diamino-2-hydroxypropane (0.27 ppb) [26].

3.9. Effect of interferences

A systematic study of the interference from foreign ions on the determination of aluminium was carried out. A solution containing 500 ppb of aluminium was prepared in the presence of various concentrations of Na^+, K^+, Ca^{2+}, Mg^{2+}, Cu^{2+}, and Fe^{2+} as shown in Table 1. The results show little or no interference was observed in the presence of Na^+, K^+, Ca^{2+}, and Mg^{2+}. However, in the presence of Cu^{2+} and Fe^{2+} a lower recovery of the complex was observed due to a quenching effect of these species on the fluorescence intensity of the Al-HNMA complex.

3.10. Analytical application

The method was applied for the determination of aluminium in water samples. The recovery of the proposed method was examined by analysing water samples such as bottled water, well water and tap water. As shown in Table 2, all of the samples gave recoveries ranging from 86.0 to 98.3%.

The validation of our proposed method was carried out by analysing a certified AA standard aluminium solution that is known to contain 1000 ppm (product number 119770 NIST SRT) of aluminium. The certified standard was appropriately diluted to give concentrations in the range 200–800 ppb. The data from our proposed method agreed very well with the values of the certified standard aluminium solution when compared using the Student's t-test. For a certified standard diluted to 300 ppb, t calculated was 1.38 ($\rho = 0.05$), and t tabulated was 2.776. Meanwhile, for a certified standard diluted to 500 ppb t calculated was 0.115.

4. Conclusion

The development of a simple, sensitive and selective fluorimetric method for the determination of aluminium ions based on their complexation with HNMA has been described. The complex was monitored at λ_{em} = 450 nm and λ_{ex} = 385 nm. The stoichiometry of the major complex of Al(III):HNMA is 3:1. The formation of more than one aluminium complex suggests that the method can be used for speciation studies of aluminium complexes in environmental samples. The maximum fluorescence intensity of the Al-HNMA complex was at pH 6.0 in Tris buffer. The proposed method was applied for the analysis of aluminium ions in water samples and was found to exhibit a low detection limit. The robustness of this method was checked by analysing a certified aluminium standard material, whereby excellent agreement was observed at $\rho = 0.05$ using the Student's t-test. The advantage of using HNMA as a fluorogenic ligand for the analysis of aluminium is that it exhibits attractive luminescence properties. It absorbs and emits light at relatively long wavelengths and hence will be advantageous in eliminating matrix interference from short emitting species in real samples.

Acknowledgement

The authors thank the Department of Chemistry, Sultan Qaboos University for the financial support to carry out this work.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jtusci.2015.03.009.

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