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FLUORESCENCE ENHANCEMENT OF Al3+– SODIUM MORIN–5–SULFONATE COMPLEX BY IMIDAZOLIUM IONIC LIQUID AND ITS APPLICATION IN DETERMINATION OF Al3+ IONS IN AN AQUEOUS SOLUTION
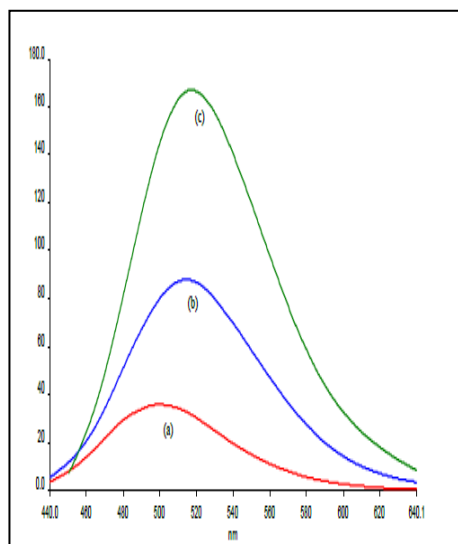
Syaza Atikah Nizar[a], Nurul Syamimi Abdul Satar[a], Shaik Azri Shaik Amar[a], Fatin Hazirah Abdullah[a], Faizatul Shimal Mehamod[b], Faiz Bukhari Mohd Suah[a*]

[a]School of Chemical Sciences, USM, 11800, Minden, Penang, Malaysia
[b]School of Fundamental Science, UMT, 21030, Kuala Nerus, Terengganu, Malaysia

Graphical abstract

Abstract

This study describes the preparation of sodium morin–5–sulfonate (NaMSA) as a new reagent for the determination of aluminium(III) (Al3+) ions based on the formation of a ternary complex. The complex consists of Al3+, NaMSA, and 1–Butyl–3–methylimidazolium hexafluorophosphate (BMIM–PF6). It was found that this method was sensitive compared to the binary complex of Al3+ and NaMSA. The ternary complex was excited at 420 nm, and the fluorescence signal was measured at 518 nm. Maximum fluorescence signal produced at pH 5.0 (acetic acid–acetate buffer), with 0.02% v/v BMIM–PF6 and 1.0×10^{-4} molL^{-1} of NaMSA. The calibration graph in linear up to 10 mgL^{-1} with the calculated detection limit of 0.017 mgL^{-1}. Effect of foreign ions towards the ternary complex was also studied. Finally, the method was applied in the determination of Al3+ ions in water samples, and satisfactory results were obtained.

Keywords: Aluminium determination, fluorescence analysis, ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate, sodium morin-5-sulfonate

Abstrak

Kajian ini membincangkan penyediaan natrium morin-5-sulfonat (NaMSA) sebagai reagen baharu bagi penentuan ion aluminium(III) (Al3+) berasaskan kepada pembentukan kompleks ternari. Kompleks ini terdiri daripada ion Al3+, NaMSA dan 1-butil-3-metilimidazolium heksafluorofosfat (BMIM-PF6). Didapati kaedah ini lebih sensitif berbanding kompleks binari Al3+ dan NaMSA. Kompleks ternari teruja pada 420 nm dan isyarat pendarfluor diukur pada 518 nm. Isyarat maksimum pendarfluor terhasil pada pH 5.0 (penimbal asid asetik-asetat), dengan 0.02% v/v BMIM–PF6 dan 1.0×10^{-4} molL^{-1} NaMSA. Graf kalibrasi adalah linear sehingga 10 mgL^{-1} dengan had pengesanan 0.017 mgL^{-1}. Kesan ion penganggu terhadap kompleks ternari turut dikaji. Akhir sekali, kaedah ini telah digunakan bagi penentuan ion Al3+ dalam sampel air dan keputusan yang memuaskan diperolehi.

Kata kunci: Penentuan aluminium, analisis pendarfluor, cecair ionik, 1-butil-3-metilimidazolium heksafluorofosfat,

1.0 INTRODUCTION

Aluminium (III) ions (Al^{3+}) is the most distributed metal in the environment, and known to be toxic to a wide range of aquatic organisms under certain conditions [1,2]. In the atmosphere, the level of Al^{3+} ions generally ranges from 0.005 to 0.18 mgm^{-3} [3]. Many foods contain Al^{3+} ions because they are grown in soil that contains Al^{3+} ions. Normally, Al^{3+} ion is solubilized in soil water, but when the pH of the soil is lower than 4.5–5.0, water is absorbed by the plant roots [4]. Al^{3+} ions can also be found in freshwater. At average neutral pH level, Al^{3+} ions concentration was reported to be lower than 10 μgL^{-1} [5]. The World Health organization (WHO) guideline value for Al^{3+} ions in drinking water is set at 200 μgL^{-1}. In humans, the highest level of Al^{3+} ion is found in the bones, while the brain has the lowest level of Al^{3+} ions [6, 7]. It has been reported that with increasing age, the concentration of Al^{3+} ions in the lungs, liver, kidneys, and brain also increase [8]. For the purpose of analysis, the total amounts of Al^{3+} ions are normally measured by means or atomic absorption spectrophotometry (AAS), graphite furnace atomic absorption (GFAAS), inductively coupled plasma (ICP), or spectrophotometry after digestion. However, it has been found that spectrophotometry and spectrofluorimetry are the most suitable due to their simplicity, high precision and accuracy, high sensitivity, and low cost [9, 10].

Morin is a flavonoid, and has been used in analytical chemistry to determine the presence of metal ions in solutions. However, the use of this compound is limited because it is insoluble in water. On the other hand, the sulfonate derivative of morin is soluble in water, and is able to form a complex with metal ions in water solutions. In addition, the formation of sulfonate derivatives of morin can result in an increase in acidity of the ligands, which is an advantage for the hydrolysis reaction [11].

Room temperature ionic liquids (RTILs) are typically salts with large nitrogen or phosphorus containing organic cations with linear alkyl chains [12]. The most common RTILs are composed of unsymmetrically substituted nitrogen–containing cation for example imidazole, pyrrolidine, and pyridine with inorganic anion such as Cl^-, PF_6^- and BF_4^- [13]. RTILs have their own advantages such as negligible vapour pressures, and they do not evaporate under normal conditions unlike organic molecular solvents. In addition, RTILs also have high thermal stability, capacity to dissolve many chemicals, high electrical conductivity, non–flammable, and are recyclable [14]. RTILs also have a wide range of solubility and miscibility than other organic molecule solvents, and can be used as a reagent and catalyst for numerous chemical reactions. In terms of application, RTILs have been utilized for separations and extractions of chemicals from aqueous and molecular organic solvents [13].

The objectives of this research are to study the reaction between sodium morin–5–sulfonate (NaMSA) and Al^{3+} ions, and to evaluate the influence of RTILs to the Al^{3+}– NaMSA complex in different conditions such as ~~the~~ optimum pH, concentration of NaMSA, concentration of ionic liquids, and interferences from other metal ions. Finally, the system was also used to determine the presence of Al^{3+} ions in real water samples. The function of RTILs in this experiment is to enhance the capability of NaMSA to attract Al^{3+} ions in order to form a new ternary complex.

2.0 METHODOLOGY

2.1 Instrumentation

Fluorescence spectra were obtained using Perkin–Elmer LS55 fluorescence spectrometer operated with 5.0 nm for excitation, and emission slits.

2.2 Chemicals

The reagents used in this experiment were aluminium potassium sulphate dedocahydrate (Merck), morin (Fluka), 1–Butyl–3–methylimidazolium hexafluorophosphate (Merck), acetone (QReC), acetic acid (QReC), concentrated sulphuric acid (QReC), sodium acetate (Merck), sodium hydroxide (R&M) and sodium chloride (Merck).

2.3 Synthesis of Sodium Morin–5–sulfonate (NaMSA)

Firstly, 40.0 mL of concentrated sulphuric acid was added to 10 g of morin. The solution was heated for 4 hours, and continuously stirred. Then the solution was cooled, and the pH value of the solution was changed to pH 3.0 by adding 20% of aqueous sodium hydroxide (NaOH) followed by adding 50.0 mL of concentrated sodium chloride (NaCl). Yellow precipitated was formed, and the product was filtered. The formula of NaMSA is $C_{15}H_9O_{10}SNa.2H_2O$.

2.4 Preparation of Stock Solution 5.00×10^{-3} M of NaMSA

NaMSA (0.22 g) was dissolved in 100 mL of volumetric flask and filled up with distilled water until mark. After that, the solution was diluted into some of the concentration needed.

2.5 Preparation of Buffer Solution

Buffer solutions were prepared based on acetic acid and sodium acetate buffer system. The buffer solutions prepared were pH 4.0, pH 4.5, pH 5.0, pH 5.5, pH 6.0, pH 6.5, and pH 7.0.

2.6 Preparation of Ionic Liquid, 1–Butyl–3–methylimidazolium Hexafluorophosphate (BMIM–PF$_6$)

The ionic liquid is slightly dissolved in water. Therefore, the ionic liquid was prepared by dissolving it in acetone. The solution was diluted from 0.2, to 10.0 % v/v.

2.7 Preparation of Spike Samples

The sample consists of tap water and pond water. First, the sample was filtered to separate impurities in the water. Next, 20 mL of the filtered water sample was added into a 50 mL volumetric flask and topped up with 1.0 mgL^{-1} of spiked Al^{3+}. The steps were repeated with 2.0 mgL^{-1}, and 3.0 mgL^{-1} of spiked Al^{3+}, respectively.

2.8 General Procedure

The fluorescence spectra of Al^{3+}–morin, Al^{3+}–NaMSA, and Al^{3+}–NaMSA–BMIM–PF$_6$ complexes were measured using a fluorescence spectrometer. Both excitation, and emission slits were fixed at 5.0 nm width.

The spectrum of the ternary complex of Al^{3+}–NaMSA–BMIM–PF$_6$ was obtained by mixing 2.0 mL of Al^{3+}, followed by 4.0 mL of NaMSA, 5.0 mL of BMIM–PF$_6$, and 3.0 mL of buffer solution. The solution was diluted into a 25 mL volumetric flask, and then filled up with distilled water until mark. The solution was shaken immediately to measure the fluorescence spectrum. The fluorescence intensity was measured at 518 nm with excitation at 420 nm.

The effect of pH, concentration of NaMSA, concentration of ionic liquid (BMIM–PF$_6$), and interference of other ions towards the ternary complex were studied. Finally, the method was used to determine the concentration of Al^{3+} ion in real water samples.

3.0 RESULTS AND DISCUSSION

The reaction of morin with concentrated sulphuric acid, and sodium hydroxide at 80^{0}C produced a new derivative of morin, which is NaMSA [11]. The chemical formula of NaMSA is C$_{15}$H$_9$O$_{10}$SNa.2H$_2$O. The deprotonated process occurred at carbon 5' because that carbon has lower steric hindrance compared to other carbons, and also due to the orientation effects in substituted benzenes. NaMSA was used for determination of Al^{3+} ion based on the formation of ternary complex. The complex consists of Al^{3+} ion, NaMSA and BMIM–PF$_6$. Figure 1 shows the reaction of the formation of ternary complex of Al^{3+}–NaMSA–BMIM–PF$_6$ complex.
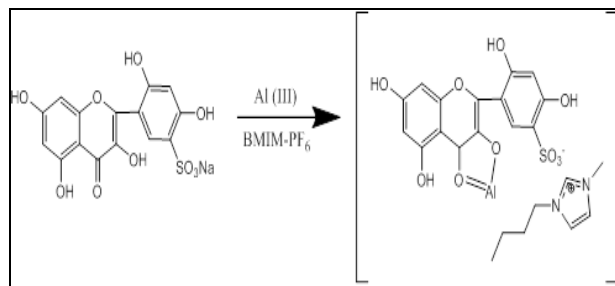

Figure 1 The proposed scheme reaction of NaMSA with Al^{3+} and BMIM–PF$_6$

Figure 2 shows the spectra of Al^{3+}–morin complex solution, Al^{3+}-NaMSA complex solution, and Al^{3+}–NaMSA–BMIM–PF$_6$ complex solution at pH 5.0, and 25℃. The formation of the ternary complex was confirmed by the shift of wavelength of the maximum emission (red shift) [15]. Maximum emission of Al^{3+}–morin complex occurred wavelength of 500 nm. Whereas the Al^{3+}–NaMSA and Al^{3+}–NaMSA–BMIM–PF$_6$ produced maximum emission at 515 nm and 518 nm, respectively. Addition of BMIM–PF$_6$ to the binary complex of Al^{3+}–NaMSA produced a significant hyperchromic shift in the ternary complex.
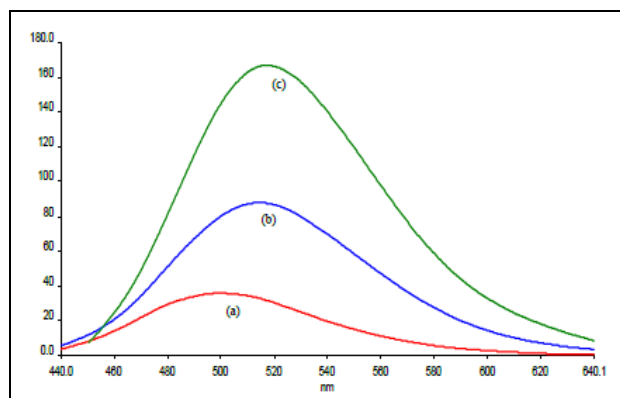

Figure 2 Emission spectra of (a) Al^{3+}–morin, (b) Al^{3+}–NaMSA, (c) Al^{3+}–NaMSA–BMIM–PF$_6$. Condition: [Al^{3+}] = 2.0 mgL^{-1}, [morin] = 3.0 × 10^{-5} mgL^{-1}, [NaMSA] = 1.0 × 10^{-4} mgL^{-1}, [BMIM–PF$_6$] = 0.02% v/v, pH = 5.0

Whenever BMIM–PF$_6$ was added to the Al^{3+}–NaMSA, the intensity of the fluorescence increased two–fold. The intensity increased from 87.91 a.u. to 167.22 a.u. This shows that the addition of ionic liquid to the metal–ligand can increase the intensity of the fluorescence. This is because BMIM–PF$_6$ is able to attract more Al^{3+} ions to form a ternary complex due to sensitization of Al^{3+}–NaMSA complex by fluoride ion of the ionic liquid. In addition, BMIM–PF$_6$ used in this study is also able to form a non-aqueous environment that is capable of incorporating the analytes into their core structure [16]. As a consequence, Al^{3+} will easily form more complex with NaMSA thus increasing fluorescence intensity of the ternary complex.

The effect of pH, concentration of NaMSA, and concentration of BMIM–PF$_6$ were also studied. The influence of the pH was studied by fixing the concentration of Al^{3+} ion and NaMSA. The fluorescence intensity gives maximum emission at pH 5.0. When the solution is more acidic (pH ≤ 3.0), the emission value is lower because the kinetic effect is very slow. A similar effect occurs when the condition is more basic (pH ≥ 8.0). It is because the hydrolysis reaction between the Al^{3+} ions with OH$^-$ ion that is present in the basic solution will decrease the reaction between Al^{3+} ion and NaMSA [16]. Therefore, pH 5.0 was chosen because it provided the greatest fluorescence intensity.

The optimum concentration of NaMSA obtained to form the ternary complex is 1.0×10^{-4} M, by fixing the concentration of Al^{3+} ion (1.0 mgL^{-1}), and BMIM–PF$_6$ (2.0 % v/v). This optimum concentration range was achieved due to the fact that this amount of NaMSA concentration is enough to yield the Al^{3+}–NaMSA complex with the BMIM–PF$_6$. The higher concentration of NaMSA gives lower fluorescence intensity due to the self–quenching effect, where ions are likely to collide with each other, and possibly the inner filter effect [15, 17].

BMIM–PF$_6$ is one of the RTILs that is based on cationic and anionic surfactant [18]. It is able to enhance the fluorescence intensity of the metal–ligand complex by creating a ternary complex. Therefore, BMIM–PF$_6$ was selected for this study. In Figure 3, it can be seen that optimum concentration of BMIM–PF$_6$ was obtained at 0.02% v/v. This is because at that concentration, it produces the highest fluorescence intensity compared to other concentrations. This is due to the fact that there is enough BMIM–PF$_6$ concentration to facilitate the reaction between the metal-ligand complex. Hence 0.02% v/v BMIM–PF$_6$ was selected as the optimum concentration, and was used for further studies.
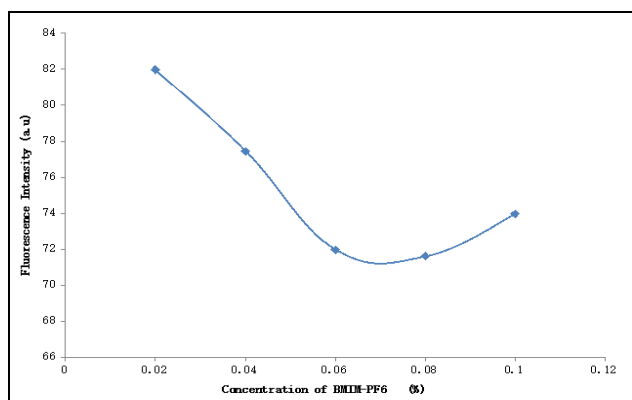

Figure 3 Effect of BMIM–PF$_6$ concentration on the fluorescence intensity. Condition: [Al^{3+}]= 1.0 mgL^{-1}, [NaMSA] = 1.0×10^{-4} mgL^{-1}, pH = 5.0, at 518 nm

The order of reagent addition has a significant effect on fluorescence intensity. This procedure assures a complete and fast development of the fluorescence for the ternary complex. The effect was studied by varying the order of reagent added. It was found that an initial formation of a weak fluorescent binary complex of Al^{3+}-NaMSA must be carried out. The previous formation of the fluorescence binary complex of Al^{3+}-NaMSA facilitates efficient incorporation of BMIM-PF$_6$ to form the ternary complex, thus a shorter time is needed to achieve a full fluorescence development. Other combinations of binary complexes (Table 1) produced a non-fluorescent binary complex except for NaMSA-Al^{3+} binary complex. However, the fluorescence intensity produced is lower than Al^{3+}-NaMSA complex. So, this order was chosen and was applied throughout the experiment.

Table 1 Fluorescence intensity of various reagent orders

Reagent order	Fluorescence intensity (a.u.)
Al^{3+}–NaMSA–BMIM–PF$_6$	167.22
NaMSA–BMIM–PF$_6$–Al^{3+}	110.60
Al^{3+}–BMIM–PF$_6$–NaMSA	109.20
NaMSA–Al^{3+}–BMIM–PF$_6$	102.88
BMIM–PF$_6$–Al^{3+}–NaMSA	96.50

From this experiment, the normalized calibration graph of Al^{3+} concentration versus relative fluorescence intensity ($(I_0-I)/I_0$) was plotted, and is shown in Figure 4, where, I was the measured fluorescence intensity at any Al^{3+} ion, and I_0 was the intensity of blank solution. The Al^{3+}–NaMSA–BMIM–PF$_6$ complex exhibited a linear emission based response to Al^{3+} ion in the concentration range of 1.0 mgL^{-1} to 10.0 mgL^{-1} with detection limit of 0.017 mgL^{-1} and the relation correlation coefficient, R^2 = 0.984.
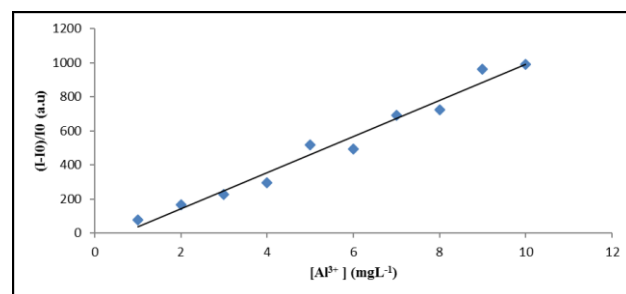

Figure 4 Normalized concentration range calibration graph for Al^{3+}–NaMSA–BMIM–PF$_6$ complex system. Condition: [NaMSA] = 1.0×10^{-4} mgL^{-1}, [BMIM–PF$_6$] = 0.02% v/v, pH = 5.0

The effect of foreign ions towards the ternary complex was also studied. A sample containing 1.0 mgL^{-1} Al^{3+} ion was prepared in the presence of 1.0 mgL^{-1} of Fe^{3+}, Cu^{2+}, Zn^{2+}, EDTA, PO$_4^-$ and F$^-$. The results shown in Table 2 indicate little interference is observed in the presence of Fe^{3+}, Cu^{2+} and Zn^{2+}. However, the presence of PO$_4^-$, F$^-$ and EDTA showed

a strong interference because they are known to form a stable complex with Al^{3+} ion [16]. However, these interferences can be reduced or eliminated by increasing the mole ratio of the interfering species. Another option is to use a masking agent such as 1,10–phenanthroline to reduce or eliminate the interferences of Fe^{3+} and hydroxylamine for Cu^{2+}. F^- ion produces the highest interferences to the complex because it can form a very stable complex with Al^{3+} ion. Therefore, a higher amount of Be(II) in the form of berilium chloride is needed in order to eliminate F^- from interfering with the ternary complex of Al^{3+}–NaMSA–BMIM–PF_6 [19, 20].

Table 2 Effect of interfering species on the recovery of 1.0 mgL^{-1} Al^{3+} ion. Condition: [NaMSA] = 1.0×10^{-4} M, [BMIM–PF_6] = 0.02% v/v

Ion	Mole ratio	Intensity (a.u.)	Intensity error	Relative error (%)
Cu^{2+}	1:1	249.31	-8.58	-3.56
Zn^{2+}	1:1	237.72	3.01	1.25
Fe^{3+}	1:1	245.36	- 4.63	- 0.02
PO_4^-	1:1	209.68	31.05	12.90
F^-	1:1	179.69	61.04	25.36
EDTA	1:1	176.48	64.25	26.69

Finally, this method was applied in the determination of Al^{3+} in real water samples. Table 3 shows the presence of Al^{3+} in the water samples. As the results obtained were satisfactory, the proposed method is considered sensitive, reliable, and could be applied for determination of Al^{3+} ion in real samples.

Table 3 The spike sample of Al^{3+}. Condition: [NaMSA] = 1.0×10^{-4} M, [BMIM–PF_6] = 0.02% v/v, pH = 5.0

Sample	Spiked Al^{3+} (mgL^{-1})	Found (mgL^{-1})
Tap water	1.0	± 1.38
	2.0	± 2.04
Pond	1.0	± 1.19
water	2.0	± 1.98

4.0 CONCLUSION

The procedure described in this research, which utilizes an extraction step in determination of Al(III) by fluorescence method, offers a substantial improvement compared to other methods. It was found that the newly prepared morin derivative, NaMSA is able to form a ternary complex with Al^{3+} and BMIM–PF_6. It also found that, the use of ionic liquid, BMIM–PF_6 increased the fluorescence intensity and sensitivity of the ternary complex. The optimum condition for the ternary complex system is obtained at pH 5.0 in the presence of 1.0×10^{-4} mol L^{-1} NaMSA and 0.02% v/v of BMIM–PF_6. A useful calibration range of 1.0 mgL^{-1} to 10.0 mgL^{-1} was obtained with the calculated limit of detection of 0.017 mgL^{-1}. The

system was then utilized to determine the presence of Al^{3+} ion in real water samples, and the results obtained are satisfactory.

Acknowledgement

References

[1]   Nayak, P. 2002. Aluminum, Impact and Disease. *Environ. Res. Sec. A.* 89: 101-115.
[2]   Wauer, G. Heckemann, H. J., and Koschel, R. 2004. Analysis of Toxic Aluminium Species in Natural Waters. *Microchim. Acta.* 146: 149-154.
[3]   Flaten, T. P. 2001. Aluminium as a Risk Factor in Alzheimer's Disease, with Emphasis on Drinking Water. *Brain Res. Bull.* 55: 187-196.
[4]   Matsumoto, H. 2000. Cell Biology of Aluminum Toxicity and Tolerance in Higher Plants. *Int. Rev. Cytol.* 200: 1-46.
[5]   Arvand, M. Kermanian, M., and Zanjanchi, M. A. 2010. Direct Determination of Aluminium in Foods and Pharmaceutical Preparation by Potentiometry using an AlMCM–41 Modified Polymeric Membrane Sensor. *Electrochim. Acta.* 55: 6946-6952.
[6]   Doll, R. 1993. Review: Alzheimer's Disease and Environmental Aluminium. *Age Ageing.* 22: 138-153.
[7]   Yokel, R. A. & McNamara. P. J. 2001. Aluminum Toxicokinetics: An Updated Mini Review. *Pharmacol. Toxicol.* 88: 159-167.
[8]   Yokel, R. A. 2000. The Toxicology of Aluminum in the Brain: A Review. *Neurotoxicology.* 21: 813-828.
[9]   Ghavami, R. Najafi, A., and Hemmateenejad, B. 2008. Chemometrics–assisted Spectrophotometric Methods for Simultaneous Determination and Complexation Study of Fe(III), Al(III) and V(V) with Morin in Micellar Media. *Spectrochim. Acta A.* 70: 824-834.
[10]   Alonso–Mateos, A. Almendral–Parra, M. J. Curto–Serrano, Y., and Rodríguez–Martín, F. J. 2008. Online Monitoring of Aluminium in Drinking Water with Fluorimetric Detection. *J. Fluoresc.* 18: 183-192.
[11]   Kopacz, M. 2003. Quercetin and Morinsulfonates as Analytical Reagents. *J. Anal. Chem.* 58: 225-229.
[12]   Freemantle, M. 2010. *An Introduction of Ionic Liquid.* Cambridge, UK: The Royal Society of Chemistry.
[13]   Anderson, J. L. Armstrong, D. W., and Wei, G. T. 2006. Ionic Liquids in Analytical Chemistry. *Anal. Chem.* 78: 2893-2901.
[14]   Wang, H. Mao, J. Duan, A. Che, B. Wang, W. Ma, M., and Wang, X. 2013. Fluorescence Quenching of 4–tert–octylphenol by Room Temperature Ionic Liquids and Its Application. *J. Fluoresc.* 23: 323-331.
[15]   Abdullah, F. H. Abdul Latif, N. A. Mohd Suah, F. B., and Mehamod, F. S. 2017. Sensitive Fluorimetric Determination of Al3+ Ion Based on the Formation of Ternary Complex Containing Room Temperature Ionic Liquid. *J. Lumin.* 188: 267-274.
[16]   Wu, H. Zhang, L. B., and Du, L. M. 2011. Ionic Liquid Sensitized Fluorescence Determination of Four Isoquinoline Alkaloids. *Talanta.* 85: 787-793.
[17]   Lakowicz, J. R. 2006. *Principles of Fluorescence Spectroscopy.* Singapore: Springer.
[18]   Wang, H. Mao, J. Li, C. Ma, M. Wang, Y. Wang, W. Zeng, A., and Wang, X. 2014. Effects of Ionic Liquids on Fluorescence Properties of 4–t–octylphenol in the

Presence Of Surfactant or β–cyclodextrin. *J. Lumin.* 149: 45-53.

[19] Ren, J. L. Zhang, J. Luo, J. Q. Pei, X. K., and Jiang, Z. X. 2001. Improved Fluorimetric Determination of Dissolved Aluminium by Micelle–Enhanced Lumogallion Complex in Natural Waters. *Analyst*. 126: 698-702.

[20]   Suah, F. B. M. Ahmad, M., and Mehamood, F. S. 2017. Effect of Non-ionic Surfactants to the Al(III)-morin Complex and its Application in Determination of Al(III) Ions: A Preliminary Study. *Mal. J. Anal. Sci.* 21: 793-800.