

Quantitative determination of Al(III) ion by using Alizarin Red S including its microspheres optical sensing material

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A facile UV-Vis spectrophotometric method for quantitative determination of Al³⁺ ion based on chromophoric Alizarin Red S (ARS) was carried out. ARS reagent was used as an organic chelator for Al³⁺ ion to form ARS–Al(III) complex. The yellow-coloured ARS changed to reddish-orange hue after reaction with Al³⁺ ion and formed ARS–Al(III) complex at optimum pH 4. ARS reagent yielded linear concentration range over 0.1–1.0 ppm Al³⁺ ion and a fast response time of ~35 s. The reproducibility study for ARS–Al(III) complex was found to give satisfactory relative standard deviation (RSD) values of 2.4–3.1%. The ARS reagent demonstrated good photostability over an 8-hour experimental period. An attempt has been conducted to physically immobilize ARS reagent onto newly synthesized photocurable poly(*n*-butyl acrylate) [poly(*n*BA)] microspheres, followed by reflectometric transduction of ion recognition event. The micro-sized poly(*n*BA) spheres has been confirmed by scanning electron microscopy (SEM). The colour change of the immobilized ARS, *i.e.* before and after reaction with Al³⁺ ion was found to be similar to the ARS solution analysis at pH 4. The acrylic-based optical microsensor showed potential to accommodate both quantitative and semiquantitative *in situ* evaluation of Al³⁺ ion concentration in environmental water and biological fluids.

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Introduction

Aluminium is the third most abundant element followed by oxygen and silicon, and it is the most abundant metal in the earth crust. About 8% by weight of the earth solid surface consists of this element. Al³⁺ ion is a toxic heavy metal ion that is frequently used industrially. The toxicity effect of Al³⁺ ion has been evidenced in many studies and the element is implicated in Alzheimer's disease and other human neurodegenerative diseases.¹ Exposure to aluminium-containing drugs, inhalation of aluminium dust and ingestion of aluminium-contaminated foods and drinks can cause toxicity in humans.² According to WHO,³ various physicochemical and mineralogical factors can significantly affect the normal Al³⁺ ion concentration in water system. About 0.01 to 0.05 mg L⁻¹ of Al³⁺ ion is usually found in near-neutral pH natural waters and it increases to the range of 0.5–1 mg L⁻¹ Al³⁺ ion in acidic waters or water rich in organic matter. Most drinking waters contain Al³⁺ ion at the ppb levels, whilst human body naturally contains 35 mg of Al³⁺ ion. However, patients with kidney failure have difficulty in

excreting excess absorbed Al³⁺ ion. Sooner or later, this can lead to serious neurotoxic disease. Therefore, it is important to closely monitor Al³⁺ ion levels in patients to avoid Al³⁺ ion levels approaching dangerous limits. Besides, aluminium is also extensively applied in the manufacturing industry such as in food packaging, antiperspirants, antacid indigestion remedies, cosmetics and beverages.⁴ Therefore, determination of very low level of Al³⁺ ion becomes increasingly demanded in environmental and clinical chemistry.

There are several analytical methods normally employed to determine Al³⁺ ion in biological and environmental samples such as inductively coupled plasma atomic emission spectroscopy (ICP-AES) and graphite furnace atomic absorption spectrometry (GF-AAS). Both of these methods are popular but present several disadvantages in serious matrix interferences. In addition, equipment required for ICP or GF-AAS methods is expensive and accurate determination of Al³⁺ ion concentration requires considerable expertise.^{5,6} Other common methods used for Al³⁺ ion determination are spectrofluorimetry⁷ and atomic absorption spectroscopy.⁸ Alison *et al.*⁹ had conducted research to determine Al³⁺ ion by using single-use chemically modified electrode (CME). The preparation method was simple merely requiring a dip-coating of high density electrode in the ARS solution. However, the electrochemical Al³⁺ ion sensor sustained interference from Cu²⁺ ions. Shu and Gang¹⁰ conducted another study to determine Al³⁺ ion by using pyrocatechol violet-modified electrode *via* indirect differential pulse voltammetry (DPV)

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method. Even though their detection system was simple it possessed certain weaknesses in terms of sensitivity and selectivity.

To overcome those problems that arose by using classical analytical techniques and electrochemical methods, an optical chemical sensor will offer better advantages over other methods. An optical sensor is compact and best suited for miniaturization while at the same time it is resistant to electrical interference and utilizes the simplicity of photometric measurement. An optical sensor is suited in this area as it may easily be incorporated into low-cost and easy-to-use kits as well as offering the good selectivity and sensitivity necessary for real-time environmental monitoring.¹¹ Reagent immobilization becomes crucially important in sensor fabrication. When a chemical reagent is immobilized into or onto a polymer matrix, it gains better stability in the immobilization matrix and so avoids the undesirable susceptibility to interference and fouling.¹²

In this study, a simple analytical technique for quantitative determination of hazardous Al^{3+} ion in aqueous environment using ARS reagent and UV-Vis spectrophotometer was carried out. A series of optimization of reactions between ARS reagent and Al^{3+} ion were conducted, such as pH effect, ARS reagent concentration effect, dynamic linear concentration range, response time, reproducibility and interference studies. Photostability was also performed to determine the ARS stability. This method has advantages such as good accuracy and precision, low cost and simple means to trace metal ion determination. ARS reagent was used herein because it is one of the most useful photometric reagents to determine metal ions and its ability to create chelates with a multitude of metal cations. Non-plasticizer poly(*n*BA) microspheres were then synthesized *via* a facile emulsion photolithography step. The morphology of the acrylic microspheres was perceived under scanning electron microscopy (SEM). Then, a reflectometric Al^{3+} ion microsensor was developed simply by mixing the ARS solution with the as-synthesized acrylic microspheres. The reflectance intensity of the Al^{3+} ion sensing microspheres was observed using a fiber optic reflectance spectrophotometer in the presence and absence of Al^{3+} ion at optimum reaction conditions.

Experimental

Preparation of ARS reagent and Al^{3+} ion solution

All chemicals used were of analytical grade and deionised water was used throughout for solution preparation. Stock solution of 0.2 mM ARS ($\text{C}_{14}\text{H}_7\text{NaO}_7\text{S}$, R&M Chemicals) was prepared by weighing 7 mg of ARS (in the form of sodium salt) and dissolved with 95% ethanol in a 100 mL volumetric flask and gently shaken. About 50 mM acetate buffer solution was prepared from 0.05 M sodium acetate (NaAc, 99%, Friendemann Schmid Chemical) and 0.05 M glacial acetic acid (HAc, 99.8%, R&M Chemicals) solutions. A standard stock Al^{3+} ion solution was prepared by dissolving the required amount of aluminium(III) nitrate ($\text{Al}(\text{NO}_3)_3$, 98%, R&M Chemicals) in the deionized water. It was then transferred into a 100 mL volumetric flask. Al^{3+} ion working solutions were prepared by proper dissolution of the

resulting 1000 ppm Al^{3+} ion stock solution using deionized water.

Instrumentation

Absorption measurements were made with a single beam UV-Vis spectrophotometer (Thermo Scientific) from 200 nm to 800 nm. A fiber optic spectrometer (Ocean Optics, model USB4000-UV-VIS) was used to measure the reflectance intensity of immobilized ARS and its complex with Al^{3+} ion. The synthesis of acrylic microsphere was prepared *via* photopolymerization process under nitrogen gas flow with the aid of a UV transmitter unit. The UV box equipped with four light tubes radiated UV light at the wavelength of 350 nm. Ultrasonic cleaner was used to sonicate the microspheres mixture. Centrifuge was used for isolation of as-synthesized acrylic microspheres. Acetate buffer solution pH was adjusted with a pH meter (Mettler Toledo).

Characterization of reactions between ARS and Al^{3+} ion

Multivariate analyses between ARS reagent and Al^{3+} ion in solution have been carried out using UV-Vis spectrophotometric method. These include pH effect, ARS reagent concentration effect, dynamic linear concentration range, response time, repeatability, reproducibility, photostability and interference studies.

pH effect was carried out by varying the pH of the acetate buffer solution from pH 3 to pH 7 for reaction between ARS and Al^{3+} ion. The study of the effect of reagent concentration was performed by varying the ARS reagent concentration in the range of 0.01–0.16 mM at pH 4 for reaction with 8 ppm Al^{3+} ion.

The dynamic linear concentration range of Al^{3+} ion was determined by varying the concentration of Al^{3+} ion solution between 0.1 ppm and 8.0 ppm at optimum pH 4 and ARS held constant at 0.15 mM. Reproducibility analysis was studied using 10 replicates of 0.3 ppm and 1.0 ppm Al^{3+} ion at pH 4 and 0.15 mM ARS. Response time study was conducted over 3 different Al^{3+} ion concentrations at 0.3 ppm, 1.0 ppm and 4.0 ppm under optimum reaction conditions, and the absorption reading was taken every 30 s for 5 min.

Photostability study was performed by continuously exposing the ARS solution at pH 4 to a light source for 8 h to examine the possible photodecomposition occurred to the reagent and the absorbance signal was recorded every one hour. Interference study using various foreign ions has been studied by introducing different amounts of interfering ions to the solution containing 0.3 ppm Al^{3+} ion concentration until a $\pm 5\%$ error in the absorption signal of ARS– $\text{Al}(\text{III})$ complex. NH_4^+ , Mg^{2+} , Cl^- , Fe^{3+} , SO_4^{2-} and Cu^{2+} ions were adopted in this interference study. These ions normally co-exist in environmental water such as river water.

Synthesis of acrylic microspheres

Poly(*n*BA) acrylic microspheres were synthesized by mixing appropriate amount of *n*BA ($\text{C}_7\text{H}_{12}\text{O}_2$, 99%, Aldrich Chemistry) monomers, 2,2-dimethoxy-2-phenylacetophenone (DMPP, 99%, Aldrich Chemistry), 1,6-hexanediol diacrylate (HDDA, 80%, Aldrich Chemistry), sodium lauryl sulphate (SDS, 95%, Scharlau

Chemie) and deionized water in a scintillation bottle. The mixture was then sonicated at 25 °C for 10 min. Then, the resulting milky white emulsion was transferred into a Petri dish and placed in an UV exposure unit to allow photopolymerization process to occur for 600 s. The photocuring process was conducted in nitrogen gas environment. After that, the resulting microspheres were transferred into a 15 mL centrifuge tube and marked up with 50 mM acetate buffer solution (pH 4). Then, the microspheres were isolated by centrifugation at 6000 rpm for 10 min. A total of three washing cycles were performed using acetate buffer solution for the acrylic microspheres to remove the unreacted chemicals from poly(*n*BA) microspheres' surfaces. The as-synthesized acrylic microspheres were then dried at room temperature for 2 h. The shape and size of the non-transparent poly(*n*BA) microspheres were investigated using SEM operating at an acceleration voltage of 8.00 kV and 5.00 k \times magnification.

Immobilization of ARS onto acrylic microspheres

Approximately 7 mg of ARS reagent was dissolved with 95% ethanol in a 10 mL volumetric flask. The resulting 0.15 mM ARS solution was then transferred into a 15 mL centrifuge tube containing the as-synthesized acrylic microspheres and left overnight to allow physical absorption process to take place. Then, the ARS-immobilized acrylic microspheres were isolated by centrifugation at 6000 rpm for 10 min. Three washing cycles were carried out using 50 mM acetate buffer pH 4 to remove the loosely bound ARS molecules.

Fabrication of optical microspheres-based Al³⁺ ion sensor

Approximately 4 mg of self-plasticized ARS reagent (ARS-immobilized acrylic microspheres) was deposited onto a circle plastic strip with a diameter of 6 mm. Optical characterization of solid-state ARS reagent was then evaluated with fiber optic reflectance spectrophotometer. The fiber optic was placed directly above the immobilized ARS and the distance between the distal end of the fiber optic and the immobilized ARS was adjusted to obtain the maximum reflectance intensity. The reflectance response of the Al³⁺ ion microsensor was measured before and after exposure to 50 ppm Al³⁺ ion at pH 4. The schematic diagram of reflectance-based Al³⁺ ion microsensor is shown in Fig. 1.

Results and discussion

Absorption spectra of ARS and ARS–Al(III) complex in solution

Absorbance spectra of ARS reagent and ARS–Al(III) complex were captured in the wavelength range between 200 nm and 800 nm. Fig. 2 illustrates the absorption spectra of ARS and ARS–Al(III) complex in solution. ARS reagent shows maximum absorbance at 430 nm, while ARS–Al(III) complex gives maximum absorbance at 488 nm in the visible region. When Al³⁺ ion reacted with the ARS molecule, the hydroxyl (–OH) functional group in the ARS molecule which acted as an auxochrome group has affected the shifting of carbonyl (C=O) chromophore peak to a longer wavelength at 488 nm as well as increasing the

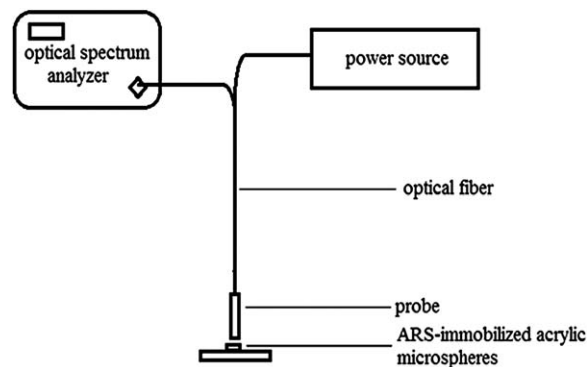
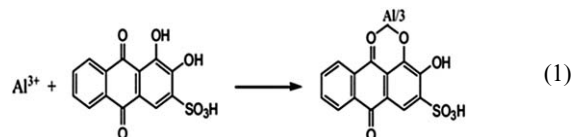


Fig. 1 Reflectance-based Al³⁺ ion microsensor.

chromogen absorbance intensity. Such a shift is called a bathochromic or red shift. As perceived by eye, the yellow-coloured ARS reagent changed to reddish orange upon interaction with Al³⁺ ion at pH 4. Sathish *et al.*¹³ reported that ARS–Al(III) complex showed red-coloured chelate around pH 4.38 at 575 nm. The chemical reaction between ARS reagent and Al³⁺ ion is shown in eqn (1). The maximum absorbance difference between the two absorbance spectra before and after reaction with Al³⁺ ion was observed at 504 nm. Thus, the subsequent quantitative studies were performed at this optimum wavelength.



Effect of pH

Characterization of pH effect was used to determine the optimum pH for the reaction between ARS and Al³⁺ ion. In this study, the reaction medium pH was varied between pH 3 and pH 7. About 0.07 mM ARS reagent was reacted with 15 ppm Al³⁺ ion in different acetate buffer pHs. Fig. 3 depicts the optimum pH was obtained at pH 4 due to the greatest absorbance difference by which an enormous divergence between ARS reagent and ARS–Al(III) complex signals occurred at 504 nm.

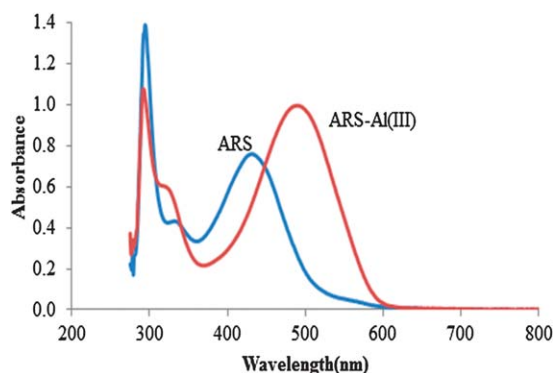


Fig. 2 Absorption spectra of ARS and ARS–Al(III) complex at 0.07 mM ARS, 15 ppm Al³⁺ ion and pH 4.

Therefore, optimum pH 4 was used for further analyses. At pH 3, lower relative absorbance signal was observed compared to pH 4, which indicated an unsuitable reaction medium for the complexation reaction between ARS reagent and Al^{3+} ion. Furthermore, a lower signal gives lower sensitivity for Al^{3+} ion quantitative analysis. The absorption difference of the ARS– $\text{Al}(\text{III})$ complex was found to be maximum under acidic conditions *i.e.* pH 4. The relative absorption value then gradually decreased when it changed towards neutral condition. The pH measurement was carried out in triplicate for each pH. Sathish *et al.*¹³ also reported that ARS reagent formed complex with Al^{3+} ion in the acetate buffer at pH 4. At pH 4, ARS formed a light yellowish-coloured solution. Some literature states that at pH below pH 5.2 most alizarin occurs in the form of yellow-coloured undissociated molecules.¹⁴ The addition of 15 ppm Al^{3+} ion concentration changed the ARS solution to a reddish orange colour. At this stage, the ARS is deprotonated, forming the charge-transfer complex. The free electrons from the chromophoric ARS transferred to the orbital d of Al^{3+} ion, where ligand covalent bonds were formed. The Al^{3+} ion : ARS ratio in the ARS– $\text{Al}(\text{III})$ complex was assumed to be 1 : 3.¹⁴ In general, ARS in the form of aqueous solution is yellow in colour (in acetate buffer, pH 5), and its color changes with pH as a result of proton dissociation.

Effect of ARS reagent concentration

ARS reagent concentration effect was conducted to determine the optimum ARS reagent concentration for the complexation reaction with Al^{3+} ion. Fig. 4 demonstrates a graph of ARS– $\text{Al}(\text{III})$ complex absorbance at different ARS reagent concentrations from 0.01–0.16 mM towards constant Al^{3+} ion concentration at 8 ppm.

The absorbance signal increased steadily with increasing ARS concentrations at the initial study and the response slowly leveled off at higher ARS concentrations and become plateau at 0.15 mM ARS. The plateau state is attributed to the most ARS reagent available has been utilized for reaction with Al^{3+} ion. Thus, the optimum concentration of the ARS reagent was obtained at 0.15 mM. Therefore, this working reagent

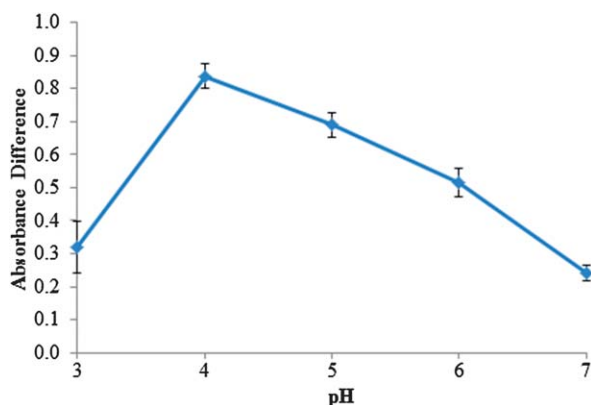


Fig. 3 The effect of pH on ARS– $\text{Al}(\text{III})$ complex formation at the wavelength of 504 nm using 15 ppm Al^{3+} ion.

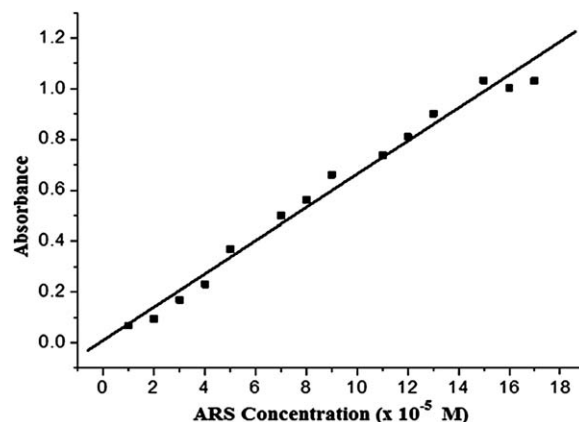


Fig. 4 Plot of absorbance versus ARS concentration from 1–16 $\times 10^{-5}$ M and 8 ppm Al^{3+} ion at pH 4.

concentration was employed for further characterizations. However, larger ARS concentrations were avoided to eliminate the chances of internal filter effect due to the maximum absorption.¹⁵ Musa and Narayanaswamy^{16,17} reported same trend for Al^{3+} ion determination using immobilized CAS/ECR through reflectance measurement.

Dynamic linear concentration range

The dynamic linear concentration range of Al^{3+} ion was determined by varying the Al^{3+} ion concentration in solution between 0.1 ppm and 8.0 ppm to react with constant ARS concentration at pH 4. Fig. 5 displays the graph of ARS– $\text{Al}(\text{III})$ complex absorbance against Al^{3+} ion concentration from 0.1–8.0 ppm at pH 4.

When the concentration of Al^{3+} ion increased from 0.1–4 ppm, the absorbance signal increased at 504 nm due to the increasing analyte ion present for the chemical reaction to occur. The optimum Al^{3+} ion was observed at 4.0 ppm, and the absorption signals remained plateau despite further addition of

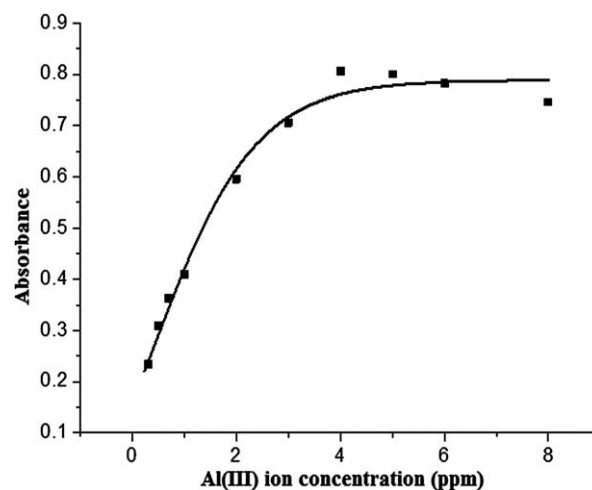


Fig. 5 Response curve obtained from ARS– $\text{Al}(\text{III})$ complex at different Al^{3+} ion concentrations in the range of 0.1–8.0 ppm at the wavelength of 504 nm and optimum pH 4.

Al^{3+} ion as almost all the ARS reagent molecules available have been reacted with Al^{3+} ion. Fig. 6 displays a calibration curve for ARS–Al(III) complex which is linear in the Al^{3+} ion concentration range of 0.1–1.0 ppm. The linear part of the plot can be described by the regression equation $y = 0.4188x + 0.1763$ with correlation coefficient, R^2 of 0.9904.

Reproducibility study

The reproducibility study was performed towards ARS–Al(III) complex to determine the reproducibility of the spectrophotometric quantitative determination of Al^{3+} ion. Reproducibility study was conducted by measuring ten different ARS–Al(III) complex solutions at the same concentration. The study was examined using 0.3 ppm and 1.0 ppm Al^{3+} ion at 0.15 mM ARS and yielded satisfactory RSD values of 2.4% and 3.1%, respectively. Fig. 7 represents the results of reproducibility study.

Response time

The response time of the ARS solution in different Al^{3+} ion concentrations *i.e.* 0.3 ppm, 1.0 ppm and 4.0 ppm had been conducted. It was observed that a faster steady state response, about 35 s was achieved when 4.0 ppm Al^{3+} ion concentration was used in the reaction with ARS to form ARS–Al(III) complex. The response time become constant after 35 s as the adjacent free Al^{3+} ions had all reacted with ARS. The presence of larger amount of analytes had increased the possibility of the analytes to react with the immobilized reagent molecules.¹⁸ This is because higher analyte concentration appears to favour faster mass transfer kinetics. Musa and Narayanaswamy¹⁶ observed the same result trend in their research on immobilization of CAS on XAD-2 resins for the determination of Al^{3+} ion. Tan *et al.*¹⁹ have also recently obtained the same pattern plot for the response time study in their research work on immobilized Riegler's reagent on XAD-7 microbeads for detection of NH_4^+ ion in environmental water samples.

For the determination of lower Al^{3+} ion concentration at 0.3 ppm, about 60 s reaction time was required to reach its steady state response. According to Safavi and Bagheri²⁰ on the

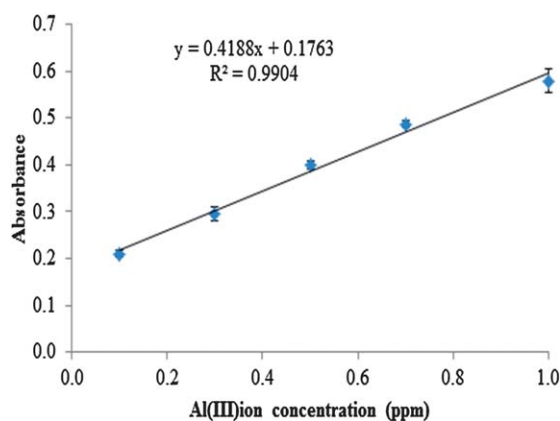


Fig. 6 Linear response of ARS–Al(III) complex in the Al^{3+} ion concentration range of 0.1–1.0 ppm at pH 4 ($n = 3$).

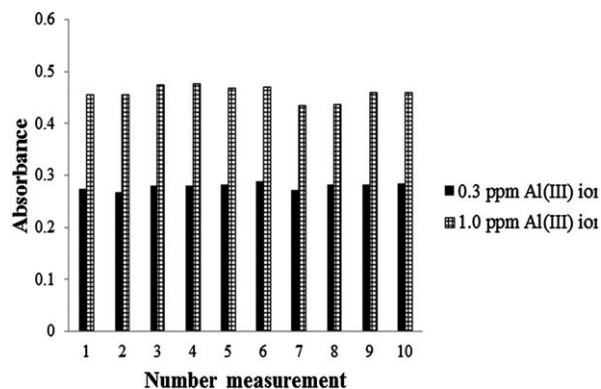


Fig. 7 Reproducibility response of ARS–Al(III) complex using 0.15 mM ARS tested over 0.3 ppm and 1.0 ppm Al^{3+} ion at pH 4.

immobilized ARS in triacetylcellulose membrane, they found that a longer response time was needed when low analyte concentration was introduced as the system must undergo three stages *i.e.* diffusion state, complex dissociation state and complex formation state. Hence, the response time was set at 35 s for the further analyses since it provided broader dynamic range and good sensitivity for the determination of Al^{3+} ion concentration. Fig. 8 shows the steady state response curves for ARS–Al(III) complex at 504 nm.

Photostability of ARS reagent

Photostability study was implemented by continuously exposing the optimum 0.15 mM ARS reagent at pH 4 to the light source for 8 h. This was done to determine the possibility of the photodecomposition of the ARS reagent upon prolonged exposure to the light source.¹⁹ The photostability study was done at ambient conditions. 0.15 mM ARS absorption was recorded every one hour interval until 8 h. The photostability RSD value obtained was 0.3%. RSD is a statistical method to measure the ARS photostability that was obtained by dividing the standard deviation of ARS absorption signal by its average signal and multiplied by 100 to express the assay as a percentage. Fig. 9 shows the absorption of ARS for 8-hour analysis duration.

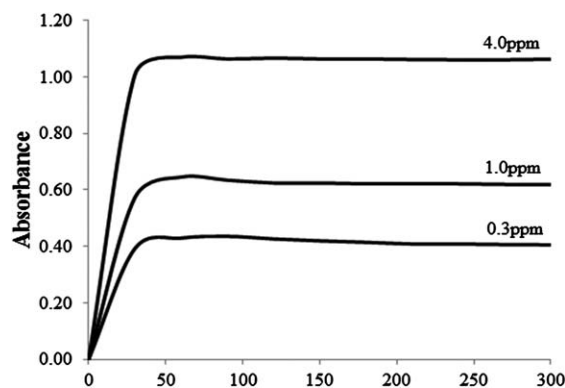


Fig. 8 Response time of 0.15 mM ARS towards different Al^{3+} ion concentrations at 0.3 ppm, 1.0 ppm and 4.0 ppm at pH 4 and wavelength of 504 nm.

It was observed that there was no significant decline in the absorbance value of ARS reagent for the time period of 8 h. This implied that the ARS reagent phase was stable against light exposure at pH 4 and room conditions. An alternative step to improve the reagent photostability is through immobilization step *e.g.* sol-gel entrapment method or covalent binding. Cajlakovic *et al.*²¹ had attempted a research study on the stability of optic pH sensor based on cross-linking poly(vinyl alcohol) (PVA) copolymer. They used sol-gel process incorporated with PVA which gave improvement for photostability response in highly flexibility and reduced gel-shrinking.

Interference study

To confirm the usefulness of this proposed method, the possible interference effect in the determination of Al³⁺ ion was evaluated. The effect of the foreign ions on the ARS–Al(III) complex is summarized in Table 1.

Under optimum conditions, foreign ions in various concentrations were added to the reaction solution (pH 4) containing 0.3 ppm Al³⁺ ion and the absorbance signals at 504 nm were measured separately. The increasing amount of interfering ion was slowly introduced into the ARS–Al(III) complex solution until the tolerance ratio of each interfering ion was taken as the largest amount yielding $\pm 5\%$ relative error at the wavelength of 504 nm.

Interference from Fe³⁺ and Cu²⁺ ions^{22,23} was expected because of their potential to form complexes with ARS reagent. The most severe interference was Fe³⁺ and Cu²⁺ ions. Fe³⁺ ion interfered significantly because Fe³⁺ ion exists as a coloured transition metal ion and it has turned the ARS–Al(III) solution brownish.²⁴ Cu²⁺ ion showed high interference effect as reddish colour ARS–Cu(II) complex was formed.²⁵

Generally, positive interference occurs when cations react with reagent molecules and cause the absorption at optimum wavelength to increase. For negative interference, it is ascribed to the anions reacting with analyte ions so decreasing the maximum absorbance signal.

In order to eliminate the interference effect from Fe³⁺ ions, ascorbic acid is suggested as a masking agent, and has been

Table 1 Tolerable interference effects of Mg²⁺, NH₄⁺, Cl[−], SO₄^{2−}, Cu²⁺ and Fe³⁺ ions on the determination of 0.3 ppm Al³⁺ ion at pH 4 and wavelength of 504 nm (*n* = 3)

Interfering ion	Tolerable molar ratio of foreign ion to Al ³⁺ ion
Mg ²⁺	250
NH ₄ ⁺	150
Cl [−]	200
SO ₄ ^{2−}	80
Cu ²⁺	0.2
Fe ³⁺	0.1

used by Costa *et al.*²⁶ to mask Fe³⁺ ion upon UV-Vis spectrophotometric determination of tin(IV) ion using pyrocatechol violet reagent. Other ions such as Mg²⁺, NH₄⁺, Cl[−] and SO₄^{2−} have almost no influence on the determination of Al³⁺ ion in this study.

SEM characterization of poly(*n*BA) microspheres

Fig. 10 shows a typical SEM image of the acrylic microspheres demonstrates the smooth surface of the microspheres with average sphere diameter at approximately 2 μ m. Novel polymeric precursor of poly(*n*BA) microspheres yielded smaller size and larger surface area simply *via* photopolymerization method.

Poly(*n*BA) microspheres as immobilization matrix

Poly(*n*BA) microspheres were functionalised as an immobilization matrix in this study. This polymeric material was chosen because of its promising properties such as small size, inertness, stability, hydrophobic and non-ionic properties. The micro-sized acrylic spheres improve the performance of the sensor as the small-sized polymer spheres provide larger surface area for adsorption of a greater amount of reagent molecules.²⁷

In this study, immobilized ARS on the poly(*n*BA) microspheres *via* physical adsorption for optical sensing of Al³⁺ ion was conducted. Fig. 11 illustrates the reflectance spectra of immobilized ARS and ARS–Al(III) complex on acrylic

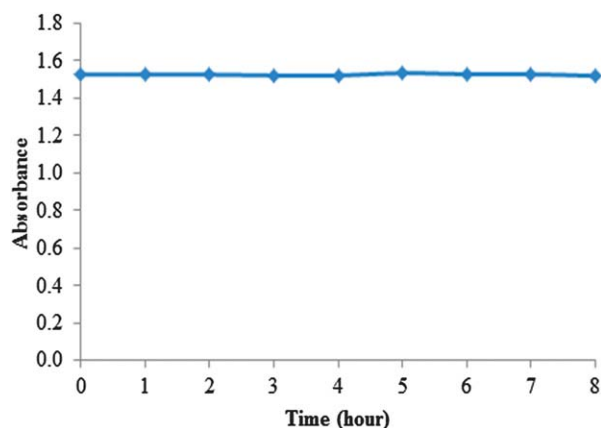


Fig. 9 Photostability profile of ARS reagent at 0.15 mM for 8 h period.

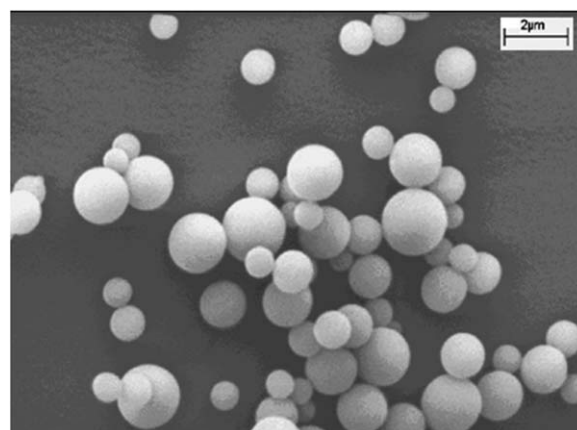


Fig. 10 SEM image of acrylic microspheres.

microspheres at pH 4. Immobilized ARS on the acrylic microspheres showed yellowish colour and changed to light orangish red after the addition of 50 ppm Al^{3+} ion. The formation of reddish orange immobilized ARS- $\text{Al}(\text{III})$ complex absorbed the incident light and attenuated the reflectance signal over the visible wavelength range. This is in contrast to the light yellow-coloured immobilized ARS whereby a higher reflectance signal was attributed to the diffuse reflection effect.

Excessive amount of *n*BA monomer yielded soft and weak polymer which can decrease the lifetime of the sensor due to the poor adhesion characteristics. The polymer features such as glass transition (T_g) value and molecular weight distributions are the main parameters affecting the feasibility of the sensor.²⁸ The increasing amount of HDDA would increase the T_g value of the polymer and thereby deteriorate the sensor response. Therefore, the composition of *n*BA and HDDA are important to achieve a good result as it affects the performance of the sensor.²⁹

Conclusions

The proposed UV-Vis spectrophotometric procedure exhibited fast analysis measurement for assay of Al^{3+} ion by using ARS reagent. The optical chemical sensor based on immobilized ARS reagent on the plasticizer-free poly(*n*BA) microspheres is advantageous for continuous and remote *in situ* monitoring of Al^{3+} ion. Due to the small size of the sensor, only very small sample quantities are required for this analysis. Direct immobilization of chemical reagent onto acrylic microspheres coupled with fast UV lithography technique could reduce the amount of work and time for sensor preparation. The dyedoped acrylic microspheres technique enabled the detection of Al^{3+} ion concentration semiquantitatively based on a visual colour scale. The use of a less expensive plastic strip as the substrate would allow low cost in mass production. The proposed experimental methodology does not require the use of complicated covalent bonding. The proposed miniature Al^{3+} ion microsensor is a more convenient analysis when compared to laboratory-based conventional methods. The soft micro-sized poly(*n*BA) spheres have great potential for

investigation with other biological or chemical reagents to form a biological or chemical active layer to produce versatile optical microsensors.

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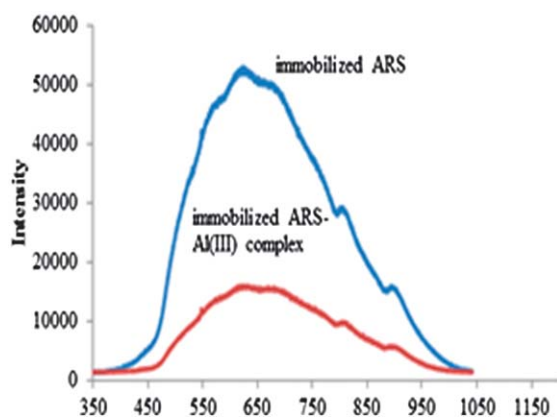


Fig. 11 Reflectance spectra of immobilized ARS and ARS- $\text{Al}(\text{III})$ complex on poly(*n*BA) microspheres at pH 4.

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