A Green Sequential Injection Spectrophotometric Approach Using Natural Reagent Extracts from Heartwood of *Ceasalpinia sappan* Linn. for Determination of Aluminium

Watsaka SIRIANGKHAWUT,*† Yaowalak KHANHUATHON, Piyanete CHANTIRATIKUL,* Kraingkrai PONHONG,* and Kate GRUDPAN****

**Creative Chemistry and Innovation Research Unit, Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Mahasarakham University, Maha Sarakham 44150, Thailand*
***Department of Chemistry, Faculty of Science, and Chemistry Research Group for Green Innovation, Center of Excellence for Innovation in Analytical Science and Technology, Chiang Mai University, Chiang Mai 50200, Thailand*

A cost-effective and environmentally friendly approach using a simple sequential injection spectrophotometric system with a non-synthetic reagent from plant extracts was proposed for a green analytical-chemistry methodology. The crude aqueous extracts from heartwood of *Ceasalpinia sappan* Linn. in acetate buffer pH 5.5 were utilized as an alternative natural reagent for the quantification of aluminium. The extracts contained homoisoflavonoid compounds, brazilin, and brazilein, which reacted with Al^{3+} to form reddish complexes with the maximum absorption wavelength at 530 nm. The optimum conditions for the sequential injection parameters, such as sequential profile, sample and reagent volumes, and the pH effect, were investigated. Under the optimum conditions, a linear calibration graph in the range of 0.075 – 1.0 mg L^{-1} Al^{3+} was obtained with limits of detection and quantification of 0.021 and 0.072 mg L^{-1} Al^{3+}, respectively. Relative standard deviations of 3.2 and 2.4% for 0.1 and 0.25 mg L^{-1} Al^{3+} (n = 11), respectively, and sampling rate of 128 injections h^{-1} were achieved. The developed system was successfully applied to pharmaceutical preparations, water, and beverage samples. The results agreed well with those obtained from the ICP-AES method. Good recoveries between 87 and 104% were obtained.

Keywords Green analytical chemistry, sequential injection, spectrophotometry, natural reagent, aluminium, *Ceasalpinia sappan* Linn.

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Introduction

Aluminium (Al) is a non-essential element that is widespread in nature, air, and water, and consequently appears throughout the food chain. Although aluminium compounds are less toxic than heavy metals, an excessive intake of Al in the human body was hypothesized as having a possible association with various diseases, such as Alzheimer's, anaemia, osteomalacia and neurological syndrome.[1,2] Aluminium is used as an antacid agent in pharmaceutical products in the form of aluminium hydroxide to neutralize or reduce stomach acid.[3,4] It is also used for cosmetics production, and in the food industry.[3] In some developing countries, the aluminium salts are used as coagulants in water-treatment plants; therefore, toxic aluminium is present in the treated water.[5] The World Health Organization (WHO) guideline for the tolerable value of aluminium in drinking water is 0.2 mg L^{-1}.[5] The Food and Agriculture Organization of the United Nation and the World Health Organization (FAO/WHO) Expert Committee on Food Additives established a Provisional Tolerable Weekly Intake (PTWI) for aluminium of 1 mg kg^{-1} body weight in 2006, which applies to all aluminium compounds in food, including food additives.[6] Therefore, an accurate determination of aluminium in water and foodstuffs is of great interest, since the content of dietary aluminium is important for both the infirm and other specific groups (*e.g.* children, pregnant women, and the elderly).

The analytical techniques commonly used for the determination of aluminium are flame atomic absorption spectrometry (FAAS),[7] graphite furnace atomic absorption spectrometry (GFAAS),[8] inductively coupled plasma-optical emission spectrometry (ICP-OES),[9] and spectrophotometry with various complexing agents such as chrome azurol S,[10,11] eriochrome cyanine R,[12] morin,[13] phenylfluorone,[14] and pyrocathecol violet.[15,16]

Recently, the development in green analytical techniques or procedures that provide economical and environmentally friendly advantages has become an important aspect in sustainable analytical chemistry.[17,18] The replacement of toxic chemicals with alternative less-harmful reagents, and the minimization of waste products using flow-based analysis

† To whom correspondence should be addressed.
E-mail: watsaka@hotmail.com
Y. K. present address: Chemistry Program, Faculty of Education, Chiang Rai Rajabhat University, Chiang Rai 57100, Thailand.

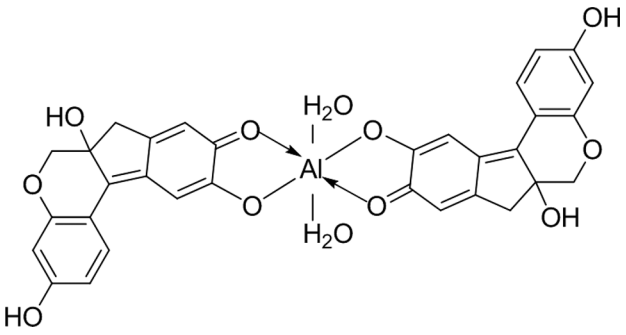

Fig. 1 Chemical structure of the Al(brazilein)$_2$ complex.

techniques are ways to achieve greener analytical methods.[19,20] The use of chemical reagents extracted from plants, *e.g.*, guava leaf extract for analysis of iron,[21] green tea,[22,23] jasmine tea,[23] and black tea[23] extracts for the analysis of Fe^{2+}, Indian Mulberry root extract[24] for the analysis of Al^{3+}, and Indian Almond leaf extract[25] for the analysis of Al^{3+} in combination with flow-based analysis techniques were reported as green analytical approaches in the literature.

The heartwood of *Ceasalpinia sappan* Linn. (Sappan wood), known locally as "Phang" in Thai, is widely used as a traditional medicine.[26] Also, the villagers in some areas, especially in the Northeast of Thailand, use the aqueous extracts of *Ceasalpinia sappan* Linn. for the dyeing of silk.[27] The extracted dyes give a beautiful red or pink color to the silk. The main compounds found in the extracted dyes are brazilin and brazilein.[28] Brazilin is readily converted to brazilein upon exposure to atmospheric oxygen and light. The stoichiometry in aqueous solution at pH 4.5 of the complex formed between Al^{3+} ions with pure brazilein extracted from heartwood of *Ceasalpinia sappan* Linn. was proposed to be 1:2 Al:brazilein.[29] For complexation, two molecules of brazilein bidentate ligands were coordinated with Al^{3+} *via* the ionized 10-hydroxyl group. Two water molecules acting as co-ligands were then coordinated to complete the octahedral arrangement of the Al(brazilein)$_2$ complex. The proposed structure of the Al(brazilein)$_2$ complex is shown in Fig. 1. However, the pure brazilein extract reagent is not yet available on the market.

Therefore, this study proposed the crude aqueous extract from the heartwood of *Ceasalpinia sappan* Linn. consisting of brazilein, as an alternative natural reagent for complexation with Al^{3+}. A sequential injection (SI) spectrophotometric system was utilized for the automated preparation and determination of sample/standard under similar conditions. This green analytical approach was evaluated for the analysis of Al^{3+} in water, beverage, and pharmaceutical samples.

Experimental

Reagents and chemicals

All chemicals used were of analytical reagent grade. Deionized water from a Simplicity 185 (Millipore, Billerica, MA) with resistivity of 18.2 M cm was used throughout the experiments. A 1000 mg L^{-1} aluminium (Al) standard solution (Merck, Darmstadt, Germany) was used for all the experimental work. Working standard solutions of Al^{3+} with different concentrations were prepared by appropriately diluting the stock solution. Hydrochloric acid (HCl, 37%) and nitric acid (HNO_3, 70%) (Univar, Ingleburn, New South Wales, Australia) were used for the digestion of the samples. Acetate buffer solutions at different pH were prepared from sodium acetate and acetic acid (Carlo Erba, Milano, Italy).

Preparation of natural reagent

Plant materials. The heartwood of *Ceasalpinia sappan* Linn. (> 5 kg) was purchased from a local retail shop in Chiang Mai Province, Thailand, in February 2012. All samples were chopped into small pieces and then dried in an oven at 50°C for 24 h. The dried heartwood was ground to a powder, and then homogeneously mixed and stored in a dry place until use.

Extraction method. The natural reagent extracted from the heartwood of *Ceasalpinia sappan* Linn. was obtained by two different procedures, boiling with water, and maceration.

Plant powder (5.0 g) and deionized water (100 mL) were mixed in an extraction flask and heated on a hotplate until boiling. The extract was boiled for 10 min. After cooling, the extract was filtered through a filter paper (Whatman® No. 4, UK) and made up to a volume of 100 mL with deionized water.

Maceration was performed with 5.0 g of plant powder and 100 mL of a solvent (ethanol, methanol, or acetone) in an extraction flask. The mixture was left at ambient temperature for 1 h. The extract was then filtered through a filter paper (Whatman® No. 4, UK) and made up to a volume of 100 mL with each extraction solvent.

Natural reagent with 1 M acetate buffer solution pH 5.5 (R-B). Sodium acetate 3-hydrate (11.50 g) was dissolved with the crude aqueous extracts from the heartwood of *Ceasalpinia sappan* Linn. Acetic acid (0.9 mL) was then added, and the solution made up to 100 mL in a volumetric flask. The pH of the solution was measured and adjusted by 1 M sodium hydroxide (NaOH) or 1 M HNO_3.

Sample preparation

Pharmaceutical samples. Five of aluminium hydroxide ($Al(OH)_3$) gel samples (P1 – P5) were obtained from local hospitals in Ubon Ratchathani Province and Khon Kaen Province, Thailand. The other samples (P6 – P10) were selected and bought directly from local drug stores in Maha Sarakham Province, Thailand. A stock solution of the suspension was prepared by following the pharmacopoeia procedures.[30] Briefly, the method involved the transfer of an accurately measured quantity of gel or fine powder (in case of tablet), equivalent to about 1.2 to 1.5 g of aluminium hydroxide to a beaker. Then, 15 mL of hydrochloric acid was added, and the mixture was heated gently until being completely dissolved. The solution was then cooled and filtered (in case of tablet), and then diluted with deionized water into a 500-mL volumetric flask.

Tap water samples. Tap-water samples were collected from the water supply network at different locations in Maha Sarakham Province, Thailand. The samples were collected in clean polyethylene bottles (1 L), and preserved to pH ≤ 2 by the addition of 2 mL of concentrated nitric acid per litre. No sample pretreatment was performed, except for filtering the sample immediately prior to analysis.

Beverage samples. The most frequently consumed brands of ten beverage samples (including carbonated beverages, vegetable/fruit juices, and ready-to-drink teas) were selected and bought directly from local superstores in Maha Sarakham Province, Thailand. All of the samples were produced in Thailand. Each sample consisted of six bottles or cans chosen at random and homogenized immediately before use. The beverage samples were digested by dry-ashing to completely destroy any organic matter. Beverage samples of 10 mL were pipetted into porcelain crucibles and the volume was reduced using a hot-plate.

Table 1 Operational step for the sequential injection system for the determination of aluminium with natural reagent extracts from the heartwood of *Ceasalpinia sappan* Linn.

Step	Valve position	Flow rate/μL s^{-1}	Volume/μL	Description
1	—	100	4000	Filling syringe with a carrier solution
2	4	75	2000	Dispensing a carrier solution to detector for recording baseline signal
3	10	50	45 (×4)	Aspiration of the natural reagent with buffer solution to HC
4	7 or 6	50	40 (×3)	Aspiration of the Al standard or sample to HC
			Sum = 300	(Steps 3 – 4 were repeated according to sequence in Fig. 2b)
5	4	75	2300	Dispense HC content towards the detector

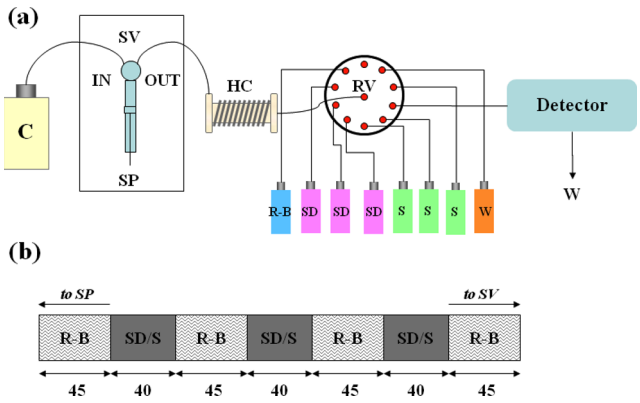

Fig. 2 Developed a sequential injection spectrophotometric system. (a) Schematic diagram of the system. (b) Sequence of solutions in a holding coil (volume of solution indicated under each zone is in microliter). C, Carrier (deionized water); R-B, natural reagent with buffer solution (pH 5.5); SD, Al standard solution; S, sample solution; W, waste; SV, switching valve; SP, syringe pump; HC, holding coil; RV, rotary selection valve

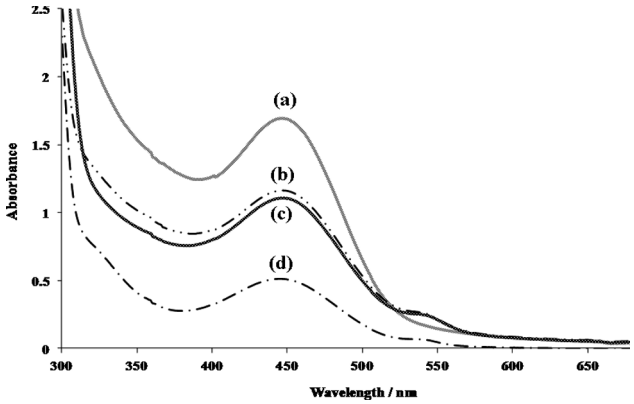

Fig. 3 Absorption spectra of the extracted solutions from heartwood of *Ceasalpinia sappan* Linn. with different solvents. (a) Methanol, (b) ethanol, (c) acetone and (d) boiling water (more details see text).

Some concentrated nitric acid was added, and the samples were evaporated until dry. Finally, the samples were ashed in a muffle furnace for 24 h at 350°C. The white ash was dissolved in 1 mL of concentrated nitric acid, transferred to a 25-mL volumetric flask, and the volume was made up with deionized water. The samples were then transferred into polyethylene bottles and stored at 4°C until further analysis.

Instrumentation and apparatus

All pH measurements were made using a 713 pH meter (Metrohm, Herisau, Switzerland). ICP-AES Optima 4300 DV (Perkins Elmer, Waltham, MA) measurements were carried out as the standard method for detection of aluminium concentration at a wavelength of 396.153 nm.

An in-house assembled sequential injection analysis (SIA) system is depicted in Fig. 2a. This consisted of a 5.0-mL syringe pump Model XL-3000 (Cavro, San Jose, CA), and a 10-port selection valve (Valco Instrument, Houston, TX). A holding coil (PTFE tubing, 0.5 mm i.d., 1.5 m long) and PTFE tubing (0.5 mm i.d.) were connected to the ports of the selection valve. A UV/VIS spectrophotometer T 80+ (PG Instrument, Leicestershire, UK) with a flow through cell (Quartz, 10 mm path length, 80 μL internal volume) was used for a spectrophotometric determination. The sequential injection system was controlled by in-house created software based on Visual Basic 6.0.[31]

Procedure

The operational sequence for the determination of aluminium by the sequential injection system is shown in Table 1. Before running the operational sequence, the holding coil (HC), the spectrophotometric flow cell (FC) and the tubing connecting to port 4 of the rotary selection valve (RV) were filled with the carrier solution (deionized water). Tubing connected to other ports of the selection valve were filled with their respective solutions. Then, the natural reagent with a buffer solution (R-B) and an Al standard (SD) or sample (S) were aspirated to a holding coil with a solution sequence, as shown in Fig. 2b. The zones were mixed and the extract with Al^{3+} complex was produced. Next, the product solution was dispensed to a flow-through cell to be detected by a spectrophotometer at 530 nm.

Results and Discussion

Extraction of natural reagent from heartwood of Ceasalpinia sappan Linn.

Type of solvent. Generally, the choice of an extracting solvent is the first important step toward parameter optimization. This has a strong impact on the yield of extraction. In this study, simple extraction methods: boiling with water, and maceration with different polar solvents, such as methanol, ethanol, and acetone were investigated. Absorption spectra in the range of 300 – 700 nm were recorded for the obtained solutions. The absorption spectra of the various extracts are depicted in Fig. 3. The results showed that the extracts from each solvent provided the highest absorbance at the maximum absorption wavelength of 440 nm. The methanol extract gave the highest absorbance, while the aqueous extracts gave the lowest absorbance. However, it would be more beneficial if the extraction could be carried out in the aqueous phase and used directly without purification.[20] Therefore, boiling with water was selected as the suitable

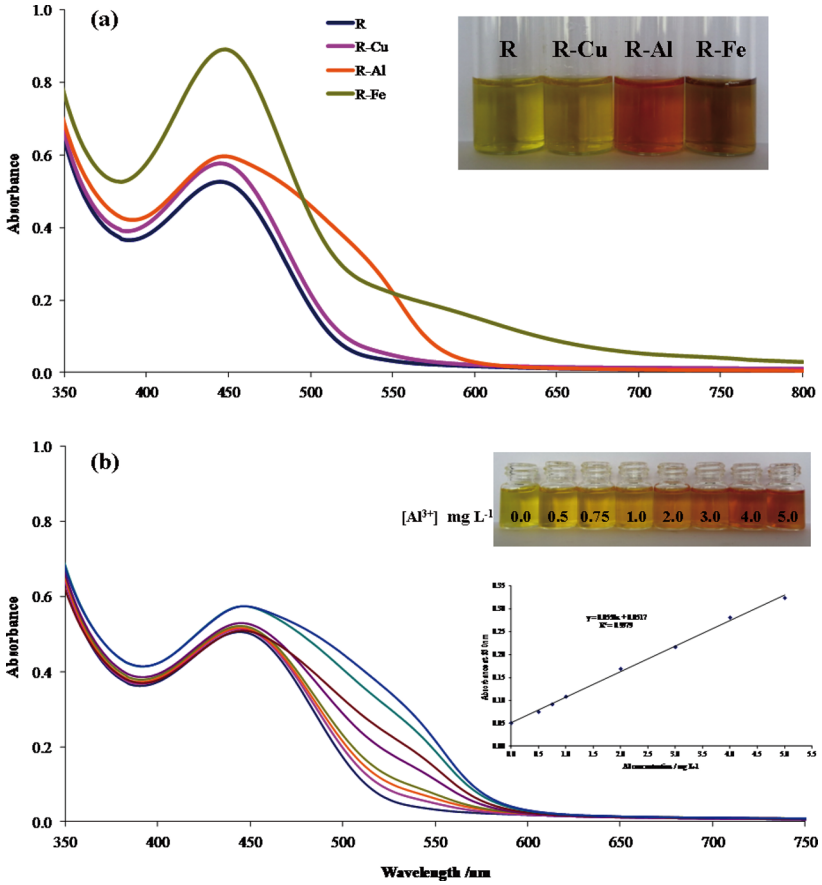

Fig. 4 Visual detection and UV-Vis spectra (a) natural reagent with some metal ions (Cu^{2+}, Al^{3+} and Fe^{3+}) at pH 4.5, (b) natural reagent at pH 4.5 with increasing concentration of Al^{3+} and calibration curve (insert graph) measured at 530 nm.

extraction method owing to its simplicity and the reduced of amounts of chemicals used.

Extraction time. The influence of extraction time on the extraction yield of natural reagent extracts from the heartwood of *Ceasalpinia sappan* Linn. using the boiling with water extraction method was investigated. The extraction time is the time (5, 10, 15, 20, 25 and 30 min) after boiling. The results indicated that the extraction yield was not time-dependent. The extraction yield reached a plateau after extraction time of 5 min. Therefore, an extraction time of 10 min after boiling was selected as suitable.

Amount of plant material. The amount of plant material related to the extraction yield was investigated by varying the weight of *Ceasalpinia sappan* Linn. heartwood powder from 1.0, 2.0, 3.0, 4.0, 5.0, and 6.0 g and extracting with 100 mL of deionized water. The absorbance at 440 nm increased with increasing amounts of plant powder from 1.0 – 4.0 g, and then remained constant. The ratio of 5.0 g of plant material per 100 mL of water was selected for the extraction procedure.

Reproducibility for extraction. To ensure the reproducibility of the various batches of natural reagent extracts for future use, the precision of absorbance of 11 batches of the extracts prepared independently was evaluated. The relative standard deviation (%RSD) for all 11 batches was 7.9%, which is an acceptable range.

Preliminary study on complexation of aluminium with natural reagent

The complex formed between Al^{3+} ions and the pure brazilein extracted from the heartwood of *Ceasalpinia sappan* Linn. was proposed as 1:2 Al: brazilein.[29] However, in this study, the crude product extracted from the heartwood of *Ceasalpinia sappan* Linn. was used without purification. Therefore, the complexation of crude extract with Al^{3+} and some other metal ions was preliminary investigated by the batch wise method.

Visual detection and UV-Vis spectrophotometric study. As shown in Fig. 4a, the mixture of the crude aqueous extracts from the heartwood of *Ceasalpinia sappan* Linn. with a buffer solution at pH 4.5 has a yellow color that exhibits light absorption in the range of 375 – 500 nm, with maximum absorption wavelength of 440 nm. After mixing the extract with other metal ions such as Cu^{2+}, Al^{3+}, and Fe^{3+}, marked changes in color were observed from yellow to darker yellow, orange and yellowish brown, respectively. However, obvious differences in absorption spectra were observed only for the mixture of crude extracted with Al^{3+} and Fe^{3+}. This result indicates the possibility of the complexation of these metals with the crude extracted from the heartwood of *Ceasalpinia sappan* Linn.

When Al^{3+} was added to the extract, the change in the color intensity was proportional to the increasing concentration. Thus, the "naked-eye" detection of aluminium was easily observed (Fig. 4b). Absorption spectra of the extract with Al^{3+} complex showed an increase of absorbance between 500 – 600 nm, with maximum absorption at 530 nm wavelength.

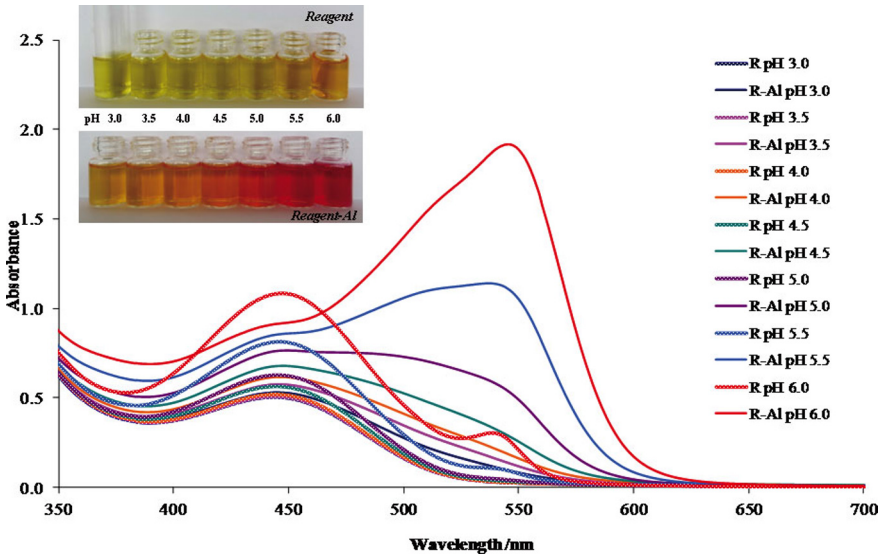

Fig. 5 Effect of the pH on complex formation of aluminium (5 mg L^{-1} Al^{3+}) with a natural reagent.

Table 2 Aspiration orders of Al^{3+} standard and reagents (n = 3)

Sequence No.	Sequence order aspiration	Volume/L	Peak height (Abs. at 530 nm) (mean ± SD)	Time/s
1	Off-line mixed	300	0.495 ± 0.007	—
2	R-B/SD	150/150	0.332 ± 0.005	20
3	R-B/SD/R-B	75/150/75	0.304 ± 0.006	22
4	R-B/SD/R-B/SD/R-B	50/75/50/75/50	0.391 ± 0.006	25
5	R-B/SD/R-B/SD/R-B/SD/R-B	25/50/50/50/50/50/25	0.411 ± 0.007	28
6	R-B/SD/R-B/SD/R-B/SD/ R-B/SD/R-B/SD/R-B/SD	(25/25)× 6	0.431 ± 0.004	37

The best linear relationship with the concentration of Al^{3+} was in the range of 0.0 – 5.0 mg L^{-1} (y = 0.0558x + 0.0517; R^2 = 0.9979, where y is absorbance and x is concentration of Al^{3+}).

Effect of pH. The reaction of 5 mg L^{-1} Al^{3+} with the extracted reagent was investigated at different pH ranges of 3.0 – 6.0 using 1 mol L^{-1} of acetate buffer. The absorption spectra at each pH were recorded. With an increase in pH, a bathochromic shift for the maximum absorption spectra of the extract with Al^{3+} occurred (Fig. 5). In addition, a marked change from yellow-orange to orange and reddish color was observed. This indicated that the complexation of Al^{3+} with brazilein in the crude extracted from the heartwood of *Ceasalpinia sappan* Linn. was proved, as recorded in the literature.[29] For this study, the pH of the solution was chosen to be 5.5 owing to its high sensitivity, and also to avoid $Al(OH)_3$ precipitate at higher pH.

SIA procedure

To achieve an automatic detection system with low chemical consumption and low waste production, the sequential injection system was developed.

Stability of natural reagent and complex. To simplify the sample preparation procedure, a pre-mixed crude aqueous extract from the heartwood of *Ceasalpinia sappan* Linn. with acetate buffer solution at pH 5.5 (R-B) was prepared; it was kept in a refrigerator at 4°C for 7 days. This R-B solution was mixed with a 5 mg L^{-1} Al^{3+} solution to test for their performance. The absorbance of the mixture was recorded after mixing for 30 min at 530 nm. The mixture of Al^{3+} and the freshly prepared extract was used for comparison. Results showed only slight decreases in the absorbance signals of Al^{3+}-natural reagent complex of less than 10% during the 72 h after preparation. This might be due to the decomposition of the active chemical species in the crude aqueous extracts during the storage time. Therefore the R-B solution could be used without losing its performance within 72 h (3 days).

Optimization of experimental parameters. To find the appropriate experimental conditions, the effects of the following two variables were investigated: sequential profile, and mixing volume ratio of sample and reagent. The highest analytical signal at the lowest value of blank, and the lowest relative standard deviation were chosen as the main criteria. Firstly, the total sample volume was varied from 50, 100, 150, 200, 250, 300, 350 and 400 µL. The analytical signal was increased with the sample volume up to 300 µL, and then only slightly increased. Therefore, a total sample volume of 300 µL was selected as optimum.

Effect of sequential profile. The effect of the sequential profiling of the solution zones (standard Al^{3+}, R-B solution pH 5.5) was investigated by creating a 300-µL total volume, using different sequence orders of solutions, as listed in Table 2. A sequence of off-line mixed (premixed) solutions was also investigated for comparison. The signals obtained from sequence numbers 5 and 6 were comparable to those obtained from off-line mixed. The reproducibility of the sequence numbers 5 and 6 were 1.70 and 0.93 %RSD, respectively. However, sequence number 6 took the longest analysis time (37 s per peak). Thus, sequence number 5 was chosen from its compromise between sensitivity, reproducibility, and analysis time.

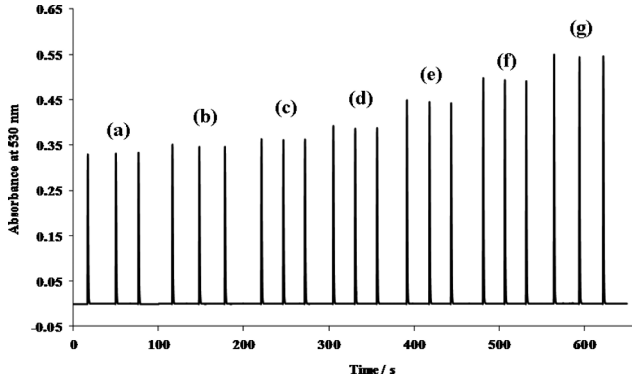

Fig. 6 SI grams of the aluminium standard at concentrations of (a) 0.000 (b) 0.075 (c) 0.10 (d) 0.25 (e) 0.50 (f) 0.75 and (g) 1.0 mg L^{-1} (conditions are described in the text).

Effect of mixing volume ratio of sample and reagent. Using sequence number 5, the concentration of natural reagent extract used was 5.0 g of heartwood/100 mL. The effect of sample and reagent volumes on the sensitivity of the system were studied at mixing volume ratios of Al^{3+}:R-B from 30:270, 60:240, 90:210, 120:180, 150:150, 180:120, 210:90, 240:60 and 270:30. The mixing volume ratio of Al^{3+}:R-B at 120:180 gave the highest sensitivity. Therefore, as presented in Fig. 2b, the aspiration volume in μL for sequence order number 5 was adjusted to 45/40/45/40/45/40/45, and then used as the optimum condition for this parameter.

Analytical features of the proposed system. The analytical characteristics of the proposed system were investigated. Using the operational sequences for sequential injection (Fig. 2b), together with the optimum conditions as described above, the standard calibration in the range of 0.075 – 1.0 mg L^{-1} was constructed by plotting peak height against the concentration of Al^{3+}. Figure 6 shows a series of SI grams obtained from the standard calibration method. Under the selected conditions, a linear calibration graph was obtained with the calibration equation $y = (0.2137 \pm 0.0004)x + (0.0033 \pm 0.0046)$, $R^2 = 0.9991$. The limits of detection ($3\sigma/s$) and quantification ($10\sigma/s$) (where σ is the standard deviation of reagent blank ($n = 11$) and s is the slope of the calibration curve) for Al^{3+} were obtained at 0.021 and 0.072 mg L^{-1}, respectively. The relative standard deviations for eleven replicate determinations of 0.1 and 0.25 mg L^{-1} were 3.2 and 2.4%, respectively. A comparable analytical performance of the proposed method with other flow-based methods for the spectrophotometric determination of aluminium, using various synthetic dyes, such as chrome azurol S (CAS),[11,32,33] eriochrome cyanine R (ECR),[34,35] and quercetin[36] was obtained, although, the developed method used only natural dye as a chromogenic reagent. In addition, the developed method provided a higher sensitivity than the previous flow-based methods using other natural reagents such as *Morinda citrifolia* root extract,[24] and *Terminalia catappa* L. leaf extract.[25] Moreover, the sample throughput of 128 injections h^{-1} was achieved with the consumption of only 0.3 mL each of sample/standard and reagent solutions per injection.

Interference study. The effect of the interfering species upon the Al-natural reagent complex was investigated using the proposed method under the optimum conditions. Various concentrations of foreign ions were spiked into a standard solution of 0.25 mg L^{-1} Al^{3+}. The interfering concentration was considered as the concentration that caused signal variations higher than ±5%. Tolerance limits of some interfering ions are listed in Table 3. Results showed that Fe^{3+} and Cu^{2+} were the major interferers with tolerance limits of 5 and 30 fold for Fe^{3+} and Cu^{2+}, respectively. However, the interfering ions may be effectively eliminated by the addition of ascorbic acid and L-histidine to the measuring solutions.[12] After adding ascorbic acid and L-histidine masking agents, the tolerance limits for Fe^{3+} and Cu^{2+} could be up to 200 and 300 fold.

Table 3 Tolerance limit of interfering ions

Interference ion	Tolerable concentration ratio
Cr^{3+}, Cl^-, PO_3^{4-}, NO_3^-, SO_4^{2-}, Mn^{2+}	> 3000
Na^+, Mg^{2+}, Zn^{2+}, Pb^{2+}	1000
Ca^{2+}	700
CH_3COO^-, Cd^{2+}	500
Ni^{2+}	250
Cu^{2+} [a]	300
Fe^{3+} [b]	200

a. After added 0.03 mol L^{-1} ascorbic acid.
b. After added 0.015 mol L^{-1} L-histidine.

Table 4 Determination of aluminium in pharmaceutical preparations ($n = 3$)

Sample[a]	Amount of aluminium/mg in 15 mL of suspension or in 1 tablet			Relative error[c], %	Recovery, %
	Added	Found	Declared[b]		
P1	0	211.3 ± 12.2	207	2.1	—
	90	291.4 ± 0.4		—	89
P2	0	217.0 ± 7.2	207	4.8	—
	90	295.0 ± 9.0		—	87
P3	0	198.1 ± 22.8	207	–4.3	—
	90	276.5 ± 15.8		—	87
P4	0	218.2 ± 28.1	207	5.4	—
	90	309.2 ± 14.0		—	101
P5	0	299.6 ± 12.6	318	–5.8	—
	130	420.4 ± 12.9		—	93
P6	0	166.1± 10.8	171	–2.9	—
	90	248.0 ± 1.3		—	91
P7	0	323.8 ± 19.9	332	–2.5	—
	180	489.1 ± 9.0		—	92
P8	0	346.2 ± 4.0	318	8.9	—
	180	528.4 ± 23.9		—	101
P9	0	234.9 ± 10.6	228	3.0	—
	250	455.6 ± 3.9		—	88
P10	0	61.3 ± 1.7	65	–5.7	—
	45	101.9 ± 0.9		—	90

a. P1 – P9, Aluminium hydroxide gel suspension; P10, aluminium hydroxide gel tablet.
b. Declared amount of aluminium in preparation.
c. Relative error = proposed method (SI) *versus* declared value.

The selectivity of the proposed method for the analysis of aluminium hydroxide gel samples was evaluated by studying their tolerance against Mg^{2+} ions that coexist as an active ingredient. The placebo mixture of magnesium hydroxide ($Mg(OH)_2$) and all excipients apart from the active ingredients in the pharmaceutical formulations[37] was used. The percentage recoveries of aluminium in the placebo mixture, and the spiked Al^{3+} ions in the placebo mixture were evaluated. Satisfactory results were obtained with no signal of Al^{3+} for the placebo mixture and 92 – 105% recoveries for the spiked Al^{3+} at 100, 250, and 500 mg L^{-1}. Thus all the active ingredients normally found in a placebo mixture did not cause any interference.

Table 5 Determination of aluminium in water and beverage samples (n = 3)

Sample[a]	Package	Amount of aluminium/mg L^{-1}			Relative error[b], %	Rec., %
		Proposed method		Reference method		
		Added	Found			
TW1	—	0	0.293 ± 0.013	0.304 ± 0.005	–3.6	—
		0.05	0.342 ± 0.018		—	98
TW2	—	0	0.245 ± 0.006	0.287 ± 0.017	–14.6	—
		0.05	0.291 ± 0.003		—	92
C1	Glass bottle	0	0.220 ± 0.009	0.199 ± 0.012	10.6	—
		0.1	0.324 ± 0.006		—	104
C2	Al can	0	0.433 ± 0.017	0.442 ± 0.011	–2.0	—
		0.1	0.522 ± 0.006		—	89
C3	Al can	0	0.722 ± 0.021	0.740 ± 0.009	–2.4	—
		0.1	0.814 ± 0.003		—	92
J1	Tetrabrik	0	0.295 ± 0.008	0.334 ± 0.012	–11.7	—
		0.2	0.473 ± 0.006		—	89
J2	Tetrabrik	0	0.342 ± 0.029	0.383 ± 0.008	–10.7	—
		0.2	0.531 ± 0.006		—	95
J3	Tetrabrik	0	0.347± 0.017	0.340 ± 0.003	2.1	—
		0.1	0.440 ± 0.006		—	93
T1	Tetrabrik	0	0.455 ± 0.013	0.472 ± 0.024	–3.6	—
		0.2	0.640 ± 0.026		—	93
T2	PET bottle	0	0.863 ± 0.009	0.894 ± 0.004	–3.5	—
		0.1	0.957 ± 0.012		—	94
T3	Al can	0	1.020 ± 0.009	1.056 ± 0.005	–3.4	—
		0.1	1.112 ± 0.003		—	92
T4	Al can	0	1.031 ± 0.025	1.063 ± 0.033	–3.0	—
		0.1	1.126 ± 0.029		—	95

a. TW1 – TW2, tap water; C1 – C3, carbonated beverage; J1 – J3, vegetable/fruit juice; T1 – T4, ready-to-drink tea.
b. Relative error = proposed method (SI) *versus* reference method (ICP-AES).

Application to real samples

The proposed system was employed for the determination of aluminium in pharmaceutical preparations, water, and beverage samples. The amounts of aluminium in aluminium hydroxide gel samples were compared with their label values. The aluminium contents of tap water and beverage samples were also analyzed by the ICP-AES method for comparison. The results are presented in Tables 4 and 5. According to t-test at 95% confident limit, the results obtained from both methods were in agreement ($t_{critical}$ = 2.080, $t_{calculate}$ = –0.397). Satisfactory recoveries in the range of 87 – 101% for pharmaceutical samples, and 89 – 104% for tap water and beverage samples were obtained.

The aluminium contents in an aluminium hydroxide gel suspension and tablet samples were found to be in the acceptable range (90.0 – 110.0%) of the labeled amount of aluminium hydroxide.[30] Aluminium concentration in the tap water samples was found to be higher than the permissible limit for drinking water of 0.2 mg L^{-1}.[5] The aluminium contents in the beverage samples was in the range of 0.220 – 1.031 mg L^{-1}. A high concentration of aluminium was found in tea beverages, because tea is one of the few plants that accumulates aluminium.[38] The concentration of aluminium found in carbonated beverages packed in aluminium cans was higher than that in glass bottles. This could be caused by the presence of carbonic acid, which corroded Al from the can wall.[39]

Conclusions

A green analytical procedure based on the sequential injection spectrophotometric system was proposed. The crude aqueous extracts from the heartwood of *Ceasalpinia sappan* Linn. can replace toxic chemical reagents for the quantitative analysis of aluminium in water, food, and pharmaceutical product samples. The proposed system significantly increased the performance of a spectrophotometric method for the determination of aluminium in terms of the cost-effectiveness, high degree of automation, and low chemical consumption. The developed system was proved to be reproducible, accurate, and rapid with a sample throughput rate of 128 injections h^{-1}. The satisfactory recovery and high sample measurement frequency proved that the proposed system has high potential as a good alternative method for monitoring the nutritional intake of aluminium in food products, and also for quality assurance of antacid suspension products in the pharmaceutical industry. In addition, the visual detection of this green approach trends to further development as a screening method for aluminium in tap-water samples, which could be useful for water-treatment plants.

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