



Reverse flow injection spectrophotometric for determination of aluminium(III)

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ARTICLE INFO

Article history:

Received 1 December 2009

Received in revised form 10 April 2010

Accepted 12 April 2010

Available online 18 April 2010

Keywords:

Reverse flow injection

Aluminium

Quercetin

Tap waters

ABSTRACT

A reverse flow injection analysis (rFIA) spectrophotometric method has been developed for the determination of aluminium(III). The method was based on the reaction of Al(III), quercetin and cetyltrimethylammonium bromide (CTAB), yielding a yellow colored complex in an acetate buffer medium (pH 5.5) with absorption maximum at 428 nm. The rFIA parameters that influence the FIA peak height have been optimized in order to obtain the best sensitivity and minimum reagent consumption. A linear relationship between the relative peak height and Al(III) concentrations were obtained over the concentration range of 0.02–0.50 mg L⁻¹ with a correlation coefficient of 0.9998. The limit of detection (LOD, defined as 3σ) and limit of quantification (LOQ, defined as 10σ) were 0.007 and 0.024 mg L⁻¹, respectively. The repeatability was 1.10% (*n* = 11) for 0.2 mg L⁻¹ Al(III). The proposed method was applied to the determination of Al(III) in tap water samples with a sampling rate of 60 h⁻¹. Results obtained were in good agreement with those obtained by the official ICP-MS method at the 95% confidence level.

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1. Introduction

Aluminium (Al) is the third most abundant element in the earth's crust and it in combination constitutes almost 8.1% by weight and is a non-essential element, to which humans are frequently exposed [1]. Al is widespread throughout nature, air, water, plants and consequently in all the food because of its uses. The main route of aluminium input to humans is through the food, drinking water, beverages, medicines, cosmetics and the use of aluminium cooking utensils. On the other hand, despite aluminium being present at low levels in natural waters, significant amounts are added to water supplies as a flocculating and coagulating agent in the purification of water and, in many cases, increasing the level of aluminium in potable water. Aluminium toxicity is well recognized as an important factor in many clinical disorders. It is a known neurotoxicant which contributes to dialysis encephalopathy syndrome and may cause Alzheimer's disease and other neurodegenerative diseases [2]. It is also associated with the mobilization of bone phosphate, and gives rise to toxicity in the hemopoietic systems in humans. The WHO guideline for the permissible level of aluminium in drinking water is only 0.2 mg L⁻¹ [3].

Several techniques such as atomic absorption spectrometry [4–8], electrothermal atomic absorption [9–15], inductively coupled plasma mass spectrometry [4,16–19], electrochemical technique [20–30], chromatography [31–34] as well as fluo-

rimetry [35–44] have been reported for determination of Al in environmental samples. However, the costs for the implementation and use of these techniques are not compatible with the resources of small laboratories. Spectrophotometric methods are widely used for Al determination due to their simplicity, rapidity, low costs and wide applications [45–47]. Many spectrophotometric methods were proposed for determination of Al(III) by using various complexing reagents such as bromopyrogallol red [48], pyrocatechol violet [49], azurol S [50], chrome azurol S [51], Morin [52], hydroxynaphthol blue [53], 2,2',3,4-tetrahydroxy-3',5'-disulphoazobenzene (tetrahydroxyazon 2S) [47], Erichrome cyanine R (ECR) [54] and 2,2',3,4-tetrahydroxy-3'-sulpho-5'-nitroazobenzene (tetrahydroxyazon SN) [55]. The above perform spectrophotometric methods for Al(III) determination are based on batch-wise methods which are time-consuming and rather large amounts of hazardous and/or expensive reagents or solvent. Flow-based methods have been replaced all batch-wise method to overcome the above problems.

A method based on the flow injection (FI) is a well-known technique that offers improvement in most batch methods, providing high sample throughput rate and simple instrumentation. Various FI spectrophotometric procedures have been described for Al(III) determination using different organic reagents. The analytical characteristics for Al(III) determination based on various chromogenic reagents using FI were compared in Table 1.

Quercetin (3,3',4',5,7-pentahydroxy-flavone) is a flavonoid compound found in plant products [62]. It is present in plant-related food including fruits, vegetables, oils, nuts, and herbs and in beverages such as wine, tea, coffee, and beer. Quercetin is a

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Table 1
The analytical characteristics of flow injection methods for determination of aluminium(III).

Method	Condition	Detection	Linear range ($\mu\text{g L}^{-1}$)	LOD ($\mu\text{g L}^{-1}$)	Reference
Lumogallion	pH 4, $\lambda_{\text{ex}} = 500 \text{ nm}$, $\lambda_{\text{em}} = 595 \text{ nm}$	Fluorometric	–	12	[57]
Chrome azurol S	pH 6.3, $\lambda_{\text{max}} = 554 \text{ nm}$, benzyltrimethyltetradecylammonium chloride (BDTAC) as surfactant	Spectrophotometric	5.4–675	3	[58]
Salicylaldehyde picolinoylhydrazone (SAPH)	pH 5.4, $\lambda_{\text{ex}} = 384 \text{ nm}$ and $\lambda_{\text{em}} = 468 \text{ nm}$	Fluorometric	5–30	5–30	[59]
Erichrome cyanin R (ECR)	pH 6, $\lambda_{\text{max}} = 535 \text{ nm}$	Spectrophotometric	150–900	16.1	[60]
Morin	$\lambda_{\text{ex}} = 410 \text{ nm}$ and $\lambda_{\text{em}} = 497.6 \text{ nm}$	Fluorometric	–	–	[61]
	Without surfactant		2–250	3.1	
	In the presence of surfactant (SDS)		2–50	2.8	
N-o-vanidillidine-2-amino-p-cresol	pH 4.0, $\lambda_{\text{ex}} = 423 \text{ nm}$ and $\lambda_{\text{em}} = 553 \text{ nm}$	Fluorometric	–	0.057	[43]
Quercetin (this work)	pH 5.5, $\lambda_{\text{max}} = 535 \text{ nm}$, CTAB as surfactant	Spectrophotometric	200–500	7	–

well-known colorimetric and also a fluorimetric reagents for determination of traces Al(III) in water and in biological samples by spectrophotometry and fluorimetry. Besides these analytical applications, the chelation of mono and polyhydroxy flavones with cations is an important factor in their bioactivity as carriers and regulators of metal concentration [34]. Recently quercetin has been used to determine Al(III) using batch-wise spectrophotometric method [63]. It has been reported for the determination of Al(III) ions in water samples. It was reported that quercetin selectively forms a stable complex with Al(III) ions and that the determination of Al(III) was relatively free from interfering species which were commonly present in water samples. To our present knowledge, no previous articles were published on rFIA procedures for Al(III) determination using quercetin as chromogenic reagent. Therefore, the complexation between Al(III) and quercetin seems promising to be adopted as a basis for the development of a rFIA method for Al(III) determination. In this work, a simple reverse flow injection (rFI) spectrophotometric procedure for the direct determination of Al(III) in tap water is developed. It is based on a reagent injection into the flowing sample solution, where Al(III) forms a complex with quercetin. Cetyltrimethylammonium bromide (CTAB) is used as a solubilizing and sensitizing agent to accelerate the reaction resulting in the higher FIA signal. Because of the high sensitivity inherent in the use of quercetin, it is decided to investigate solubilization of Al(III)–quercetin complex as the basis to develop a novel method for trace Al(III) determination with CTAB to avoid solvent extraction. The yellow colored of Al(III)–quercetin complex in micellar media is detected spectrophotometrically at 428 nm. The proposed method is tested to the determination of Al(III) in tap water samples.

2. Experimental

2.1. Reagents

All chemicals were of analytical reagent grade and were used without further purifications. All solutions were prepared with distilled deionized water.

A stock solution of 100 mg L^{-1} aluminium(III) was prepared by dissolving 7.7899 g of aluminium(III) chloride hexahydrate (Merck, Germany) in water containing 1.0 ml of concentrate hydrochloric acid (Merck, Germany) and the solution was diluted to 1 L with water. Solutions of aluminium(III) standards with lower concentrations were obtained by appropriate, accurate dilutions of this solution with deionised water.

Quercetin stock solution (1000 mg L^{-1}) was prepared from the pure product (Fluka, Switzerland) by dissolving an appropriate weight using ethanol/water mixtures (60%, v/v) as solvent. Acetate buffer solution, at a concentration of 0.1 M and at pH 5.5, was pre-

pared by dissolving 13.608 g of sodium acetate (Carlo Erba, Italy) in 500 mL of deionized distilled water in a 1000 mL volumetric flask and adjusted pH to 5.5 by using a glacial acetic acid (Merck, Germany) and diluted with water in a 1000 mL volumetric flask.

Cetyltrimethylammonium bromide (CTAB) stock solution was prepared by dissolving 9.1125 g of cetyltrimethylammonium bromide (CTAB) (Serva, Germany) in water in a 250 mL volumetric flask. The surfactant solution was prepared from stock solution of surfactant and diluted with the 0.1 mol L^{-1} of acetate buffer (pH 5.5) solution.

2.2. Apparatus

The reverse flow injection manifold consisted of a peristaltic pump (Eyela[®] MP3A, Tokyo Rikakikai Co. Ltd., Japan), with the quercetin reagent solution injected via a two-way PTFE rotary valve with a 125 μL sample loop (Rheodyne[®] model 5041, Cotati, CA). Teflon tubing (Anachem, England) with 1.52 mm i.d. was used as flow lines for Al(III) standard solutions, and CTAB in acetate buffer solution, and a Y shaped connector was used for merging the reagent streams. Mixing coils used were made from Teflon tubing (Cole-Parmer, United States) with 1.07 mm i.d. The reaction product was carried through the flow-through cell (Hellma, Germany) of a spectrophotometer (CECIL 1010 series spectrophotometer, England). An interfacing was developed to connect the spectrophotometer with a personal computer that was used as a readout device and data processing system for the proposed rFI manifold. Waterproof pH Tester 10 (Eutech Instrument, USA) was used for pH measurements.

2.3. Recommended procedure

Using the experimental setup as shown in Fig. 1, a 125 μL reagent solution containing quercetin was injected into the sample or standard stream with a constant flow rate of 2.5 mL min^{-1} via an injection valve and mixed in a reaction coil (I) (1.07 mm i.d., 75 cm long) (R_1). The injected reagent was merged with the CTAB stream at the Y junction. After the mixture was mixed with sample in a reaction coil (II) (1.07 mm i.d., 100 cm long) (R_2) where the complexation occurred. The resulting colored complex was reached the flow-through cell of the spectrophotometer where the absorbance was measured at 428 nm and displayed by the PC throughout the whole experiments. Calibration graph is obtained by plotting the increases in peak heights against various concentration of Al(III).

2.4. Sample preparation

Tap water samples were collected from several districts in Chiang Mai Province. The samples were collected in polyethylene

bottles with addition of concentrated nitric acid (1 mL concentrated nitric acid per a liter of water sample) to preserve the water samples. The samples were filtered through No. 41 Whatman filter paper into a 250 mL volumetric flask. Add 12.5 mL concentrated nitric acid and a few boiling chips. Bring to a slow boil and evaporate on a hot plate to the lowest volumes as possible (about 50 mL). After standing it to cool to room temperature, 0.625 g of thiourea, 0.1 mol L^{-1} ascorbic acid (15 mL) and 0.1 mol L^{-1} of 1,10-phenanthroline (25 mL) were added. Then, the pH of the sample solution was adjusted to 5.5 with 1 mol L^{-1} of sodium hydroxide, transferred into a 250 mL volumetric flask and made up to the mark with deionized distilled water. Finally, it was mixed well and subsequently analyzed by the proposed rFIA method.

3. Results and discussion

3.1. Preliminary investigation

3.1.1. FI manifold design

Initially a double channel FI manifold was designed and constructed using low-cost and easily available materials and equipment (Fig. 1). The manifold can be used for normal FI procedure (direct inject of the sample into the FI system) and reverse FI procedure (injection of the reagent into the FI system). In this investigation a reverse FI method was developed to reduced the reagent consumption and to improve the sensitivity for Al(III) determination. Two rFI procedure were designed as shown in Fig. 1a and b. The former rFI manifold involved injection of reagent into the sample stream in the absent marking agent whereas the latter rFI procedure involved injection of the reagent in the present of masking agent into the sample stream in order to limit the interference. It was masking agent judging from sensitivity and reproducibility. However the masking ability obtained by both methods will be investigated in the subsequent experiment.

3.1.2. Absorption spectra

The absorption spectra of the coloured complex obtained by complexation reaction between Al(III) ions and quercetin in the absence and presence of surfactant, along with their reagent blank over the range of 400–600 nm are recorded (Fig. 2). In the aqueous medium, Al(III)–quercetin complex shows the absorption maxi-

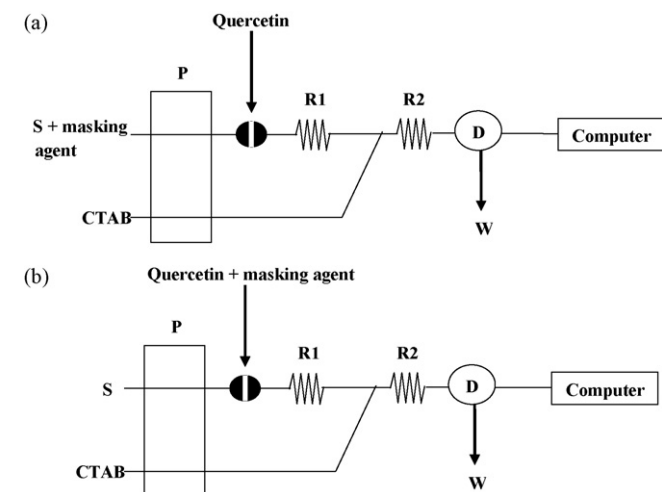


Fig. 1. rFIA manifold for determination of aluminium(III), P, peristaltic pump; S, sample; R₁, reaction coil 1; R₂, reaction coil 2; D, detector (spectrophotometer); W, waste; masking agent consisting of thiourea, 1,10-phenanthroline and ascorbic acid. (a) Injection of quercetin reagent into the sample stream in the presence of masking agent. (b) Injection of quercetin reagent in the presence of masking agent into the sample stream.

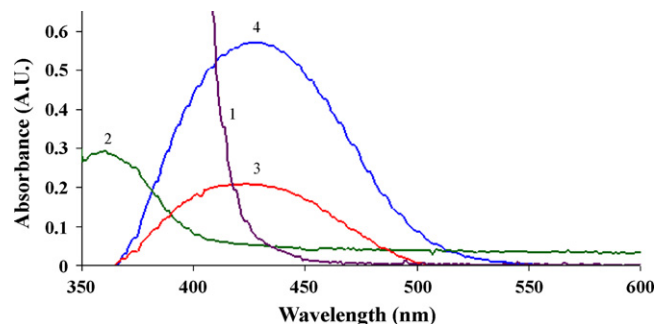


Fig. 2. Absorption spectra of quercetin (1); quercetin–CTAB (2); Al(III)–quercetin (3) and Al(III)–quercetin–CTAB (4) against reagent blank at pH 5.5. Aluminium concentration is 0.5 mg L^{-1} ; quercetin concentration is $1 \times 10^{-4} \text{ mol L}^{-1}$ and CTAB concentration is $2 \times 10^{-3} \text{ mol L}^{-1}$.

mum at 415 nm. This is probably due to the fact that addition of CTAB to Al(III)–quercetin complex results in hypsochromic shift. In presence of CTAB, Al(III)–quercetin complex has absorption maximum at 428 nm.

3.2. Optimization of the reverse flow injection system

The proposed flow system was investigated for development of an rFI procedure for Al(III) determination based on the complexation between Al(III) ions and quercetin in presence of CTAB resulting in yellow soluble complex having an absorption maximum at 428 nm. Therefore, this wavelength was chosen for the determination of Al(III) throughout further studies. The metal-to-ligand ratio was determined by the mole ratio and continuous variation method, and was found to be 1:3. The univariate optimization method (variable by variable method) was applied to select the optimum conditions for the reverse flow injection spectrophotometric determination of Al(III). The optimum value was selected by judging from the condition that gave the greatest signal, with low background signal and reasonably high reproducibility. Comparative optimization of the experimental conditions by multivariate method was also carried out.

3.2.1. Optimization of experimental variables

The optimum reaction conditions for Al(III) determination were investigated by injecting $125 \mu\text{L}$ of the quercetin reagent solution into streams of sample solution with masking agent and then was merged with the flowing stream of CTAB solution with the same flow rate of 2.5 mL min^{-1} in each channel (Fig. 1a). Using the same FI manifold, the procedure was repeated by injecting the same volume of quercetin in the presence of varying amount of masking reagent solution into the flowing stream of sample solution. After mixing at the coiled reactor (R₁) the sample plug was merged with the flowing stream of CTAB solution. The merged streams of sample and then merged with CTAB solution was carried through the coiled reactor (R₂) and reached a flow-cell in the spectrophotometer where the absorbance was measured (Fig. 1b). It was found to be more satisfactory to inject the quercetin solution into the streams of sample solution with masking agent solution (Fig. 1a) rather injecting quercetin and masking agent into the streams of sample solution (Fig. 1b) because the former method (Fig. 1a) provided the greater sensitivity than that obtained by the latter method (Fig. 1b). In addition, the effect of interference ions obtained by the former manifold was far more less than those obtained by the latter by a factor of about 1.5.

3.2.2. Effect of pH

In general, complex formation between metal ions and selected ligands are pH dependence. The complex formed by the reaction

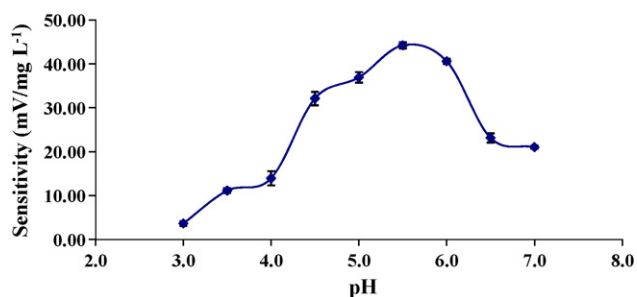


Fig. 3. The effect of pH on sensitivity.

between Al(III) standard solution and quercetin reagent should be favoured at suitable pH value. Therefore, the optimum pH for such a complexation reaction was investigated over the range of 3.0–7.0. Acetate buffer solution was mixed in solution of aluminum and CTAB. As shown in Fig. 3, it was seen that when the pH of the acetate buffer stream was adjusted to 5.5, the greatest sensitivity was obtained. Hence, pH 5.5 was chosen as optimum to obtain the desire sensitivity.

3.2.3. Effect of quercetin reagent concentration

Effect of quercetin concentrations on the determination of Al(III) ($0.05\text{--}0.25\text{ mg L}^{-1}$) was studied in the range $200\text{--}1000\text{ mg L}^{-1}$. As shown in Fig. 4a, it was indicated that the sensitivity increased with increasing quercetin concentration up to 300 mg L^{-1} when the reagent concentration was greater than 300 mg L^{-1} the sensitivity increased slightly. Therefore, a 300 mg L^{-1} quercetin solution

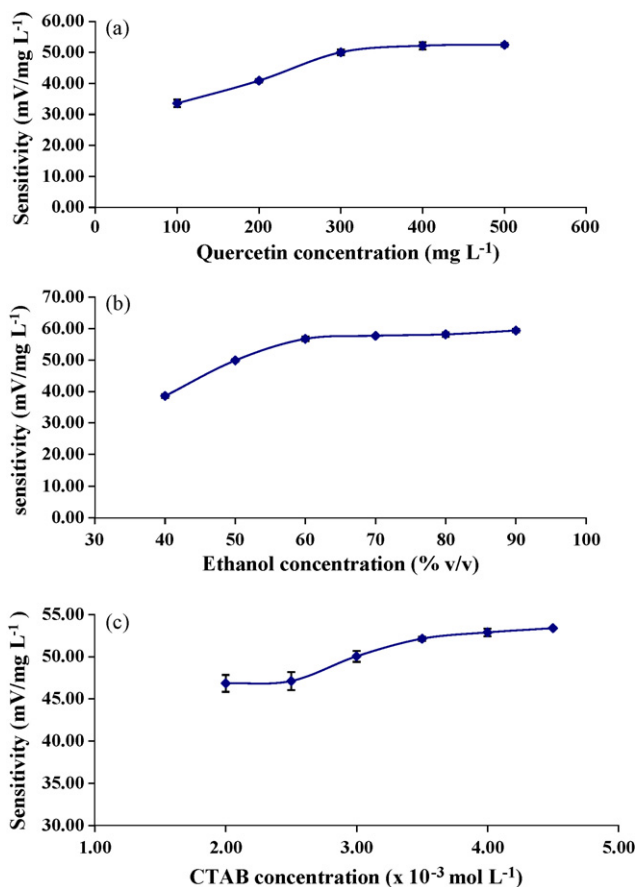


Fig. 4. The effects of reagents or solvent concentration on the sensitivity for Al(III) determination. (a) Quercetin concentration ($200\text{--}1000\text{ mg L}^{-1}$), (b) Ethanol concentration ($40\text{--}90\%$, v/v), (c) CTAB concentration (2.5×10^{-3} to $5.5 \times 10^{-3}\text{ mol L}^{-1}$).

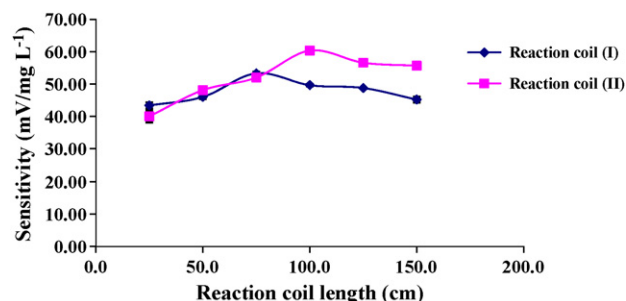


Fig. 5. The effect of reaction coils length on sensitivity.

was chosen as optimum for further experiments to avoid too high reagent consumption.

3.2.4. Effect of ethanol concentration in quercetin solution

The effect of ethanol concentration in quercetin solution was studied in the range of $40\text{--}90\%$ (v/v). The results were shown in Fig. 4b, it was shown that the greater sensitivity is obtained when the concentration of ethanol in quercetin solution increased up to 60% (v/v) after that the sensitivity increased slightly. Thus, a concentration of ethanol in quercetin solution of 60% (v/v) was chosen as optimum ethanol concentration in quercetin solution to minimize the use of organic solvent (ethanol).

3.2.5. Effect of CTAB concentration

The Effect of CTAB concentration on the determination of Al(III) was studied at different values in the range of 1.0×10^{-3} to $4.0 \times 10^{-3}\text{ mol L}^{-1}$. The results were shown in Fig. 4c. It was found that sensitivity increased very rapidly from the CTAB concentration of 1.5×10^{-3} to $2.5 \times 10^{-3}\text{ mol L}^{-1}$. After that, the sensitivities were quite constant. Consequently, a concentration of $3.5 \times 10^{-3}\text{ mol L}^{-1}$ of CTAB was chosen as optimum.

3.2.6. Effect of reaction coil(I) and coil(II) length

The effect of mixing coil(I) and mixing coil(II) lengths were studied. Teflon tubing with a fixed inner diameter (1.07 mm i.d.) but with different lengths were investigated for making mixing coil. This study was carried out at various mixing coil lengths between 25 and 150 cm for mixing coil(I) and mixing coil(II). The results were shown in Fig. 5. The optimum lengths of the mixing coil(I) and mixing coil(II) chosen for this experiment were 75 cm and 100 cm, respectively because it provide the highest sensitivity.

3.2.7. Effect of reagent flow rate

The influence of flow rate of standard and CTAB solutions were studied. The flow rates were investigated over the range $2.0\text{--}6.0\text{ mL min}^{-1}$ for both streams. The results showed that the sensitivity increased with increasing flow rate up to 2.5 mL min^{-1} . When the flow rates exceed 2.5 mL min^{-1} the sensitivity decreased because at the high flow rate gave rise to a shorter reaction time leading to smaller amounts of products. Therefore, 2.5 mL min^{-1} (Fig. 6) was regarded as the optimum flow rate and used throughout the subsequent experiments.

3.2.8. Effect of reagent volume

The reagent volume injected into the Al(III) stream has a significant effect on peak height. The effect of reagent volume on the determination of $0.05\text{--}0.25\text{ mg L}^{-1}$ Al(III) was studied by varying reagent volume of 50, 75, 100, 125 and $150\text{ }\mu\text{L}$. The results were show in Fig. 7. It was seen that reagent volume of $125\text{ }\mu\text{L}$ was the most appropriate because it gave the best sensitivity.

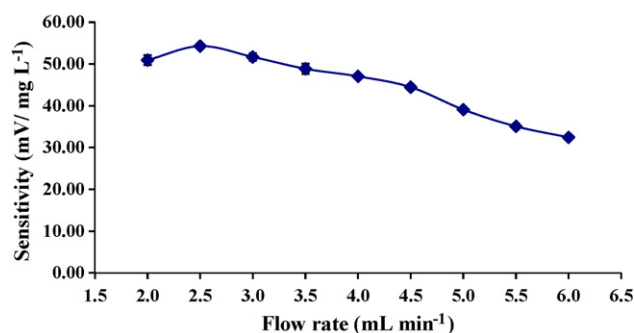


Fig. 6. Effect of flow rate on sensitivity.

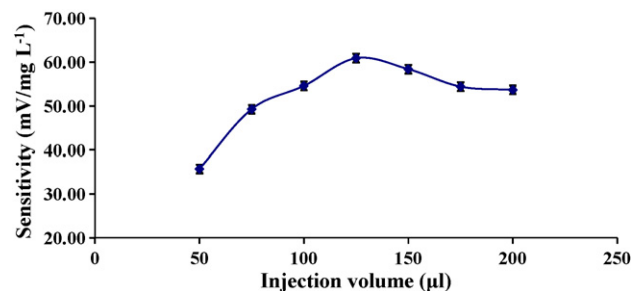


Fig. 7. The effect of injection volume on sensitivity.

3.2.9. Optimum experiment conditions for Al(III) determination

Using the so-called univariate method, it was found that the suitable experimental condition for Al(III) determination were listed in Table 2 which were rather identical with those obtained by multivariate method.

3.3. Analytical figures of merit

Using the proposed rFI manifold for Al(III) determination (Fig. 1a) under the optimum conditions (Table 2), the linear calibration curve over the range of 0.02–0.50 mg L⁻¹ Al(III) was established which can be expressed by the regression equation $y = 63.363x - 0.0246$ ($r^2 = 0.9998$) where y represents the peak height in mV and x is Al(III) concentration in mg L⁻¹ after subtraction of blank. The relative standard deviation of the proposed method (peak height in mV) calculated from 11 replicate injections of 0.2 mg L⁻¹ Al(III) was 1.10%. The detection limit (3σ) was found to be 0.007 mg L⁻¹ together with the limit of quantification limit (10σ) was 0.024 mg L⁻¹ and the mean percentage recovery of the added Al(III) of 99.9 ± 1.6 together with the sample throughput of 60 h⁻¹ were obtained ($n = 8$) moreover the advantages of the present rFI procedure were low reagent consumption (125 μL/sample), rapidity (60 h⁻¹) and free from interferences with the exception of Cu(II),

Table 2

Summarizes the optimum values of all the parameters studied in the proposed rFI method for the determination of aluminium(III).

Variable	Range studied	Optimum value
Wavelength (nm)	420–435	428
pH	3.0–7.0	5.5
Concentration of quercetin (mg L ⁻¹)	200–1000	300
Concentration of ethanol in quercetin solution (% v/v)	40–90	60
Concentration of CTAB ($\times 10^{-3}$ mol L ⁻¹)	2.5–5.5	3.5
Flow rate (mL min ⁻¹)	2.0–6.0	2.5
Reaction coil (I) length (cm)	25–150	75
Reaction coil (II) length (cm)	25–150	100
Reagent volume (μL)	50–150	125

Table 3

Summary of the interference effects of possible ions on the peak height obtained from 0.20 mg L⁻¹ aluminium ion.

Foreign ions	Tolerable concentration ratio ^a (mg L ⁻¹) of ion/Al(III)
Na ⁺ , Cd ²⁺ , Cl ⁻ , Br ⁻ , I ⁻	1000
Ba ²⁺ , Mn ²⁺ , Co ²⁺ , Ni ²⁺ , F ⁻ , NO ₃ ⁻ , SO ₄ ²⁻	500
Mg ²⁺	250
PO ₄ ³⁻ , Cr ³⁺	200
Ca ²⁺ , Zn ²⁺	100
CN ⁻	50
Fe ²⁺ ^b , Fe ³⁺ ^c , Cu ²⁺ ^d	20
NO ₂ ⁻ , HCO ₃ ⁻	10

^a The concentration of an ion is considered to be interfered when causing a relative error of more than $\pm 10\%$ with request to the signal Al³⁺ alone.

^b 0.01 mol L⁻¹ 1,10-phenantroline as masking agent.

^c 0.006 mol L⁻¹ ascorbic acid + 0.01 mol L⁻¹ 1,10-phenantroline as masking agent.

^d 0.25% thiourea as masking agent.

Fe(II) and Fe(III) which could be easily overcome by using certain masking agent.

3.4. Interferences

Effects of some possible interfering ions on the determination of Al(III) were investigated with a maximum w/w ratio of interfering solutions containing 0.2 mg L⁻¹ of Al(III) and different concentrations of some metals which might be present in waters were tested, and peak heights were measured. All cations and anions tested caused interference <10% for determining the analyte of interest. However, the most serious interferences from Cu(II), Fe(II) and Fe(III) were observed (Table 3). In order to reduce the interference levels, difference masking agents were investigated. It was clear that the possible masking agents for reducing the effects of Cu(II), Fe(II), and Fe(III) on Al(III) determination were thiourea, 1,10-phenantroline and ascorbic acid, respectively, because the interference effects could be reduced satisfactorily. Experimentally, in the absence of masking agents Cu(II), Fe(II) and Fe(III) interfered with Al(III) determination when they were present in 0.4, 0.5 and 0.1 times of the weight ratios of interfering ions to Al(III) respectively but in the presence of masking agents the tolerable weight ratios of the interfering ions to Al(III) became 50, 15 and 20 for Cu(II), Fe(II) and Fe(III) respectively.

Table 4

Validation of the proposed rFIA method for determination of aluminium(III) compare with ICP-MS method.

Water samples	Concentrations (mg L ⁻¹)		t -Test value
	rFIA	ICP-MS	
TW 1	0.270	0.273	$D = -0.010$ $SD = 0.001$ t -Test value = 2.18 t -Distribution (95%) = 2.45
TW 2	0.079	0.081	
TW 3	0.077	0.075	
TW 4	0.183	0.189	
TW 5	0.120	0.120	
TW 6	0.083	0.087	
TW 7	ND	0.011	
TW 8	0.050	0.048	
TW 9	ND	0.014	
TW 10	0.224	0.228	

ND represents not detected.

3.5. Analysis of real samples

The method developed above was applied to the determination of Al(III) in tap waters collected from 10 districts in Chiang Mai Province. After digesting the water samples with HNO₃. The results obtained were compared favorably with those obtained by ICP-MS (Table 4). The accuracy was verified by the Student's *t*-test [64] with calculated Student's *t*-test value. It was seen that experimental *t*-test value for Al(III) assay were less than the theoretical value (2.45, *n* = 8) at a confidence level of 95% (*P* value of 0.05). Reasonable agreement between the results obtained by rFI and those obtained by ICP-MS methods was found.

4. Conclusions

The proposed rFI spectrophotometric method was successfully used for determination of aluminium in water samples. This rFI method is based on complexation between Al(III) and quercetin has been developed in which a small volume of quercetin was injected into an Al(III) standard or sample stream. The optimum conditions for Al(III) determination were achieved. A linearity of the calibration graph over the range of 0.02–0.50 mg L⁻¹ was obtained with the regression equation $y = 63.363x - 0.0246$ ($r^2 = 0.9998$) with detection limit (3σ) of 0.007 mg L⁻¹ while the quantitation limit (10σ) was 0.024 mg L⁻¹. The method has been applied for the determination of Al(III) in tap water samples collected from 10 districts in Chiang Mai Province. Results obtained by the rFI method were in good agreement with the standard ICP-MS method verified by Student's *t*-test at 95% confidential level. This method was fast and reasonably economic, providing a good sample frequency of 60 h⁻¹, and should be useful for routine analysis of Al(III) in tap waters and a wide range of real samples with various sample matrices.

Acknowledgements

The authors thank the Center for Innovation in Chemistry: Postgraduate Education and Research Program in Chemistry (PERCH-CIC), the Commission on Higher Education (CHE) and the Thailand Research Fund (TRF) are acknowledged for financial support, The Royal Golden Jubilee Ph.D. program is gratefully acknowledged for the scholarship to the Ph.D. students under S. Liawruangrath's supervision. Our sincere thanks are also expressed to Department of Chemistry, Faculty of Science and the Graduate School Chiang Mai University for their partial supports.

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