



# Research Journal of Pharmaceutical, Biological and Chemical Sciences

## Quantitation of Aluminium Content in Waters and Soft Drinks by Spectrophotometry Using Eriochrome Cyanine R

Watsaka Siriangkawut<sup>1\*</sup>, Sopa Tontrong<sup>2</sup> and Piyanete Chantiratikul<sup>1</sup>

<sup>1</sup>Department of Chemistry, Faculty of Science, Mahasarakham University, Maha Sarakham 44150, Thailand.

<sup>2</sup>Faculty of Pharmacy, Payap University, Chiang Mai 50000, Thailand.

### ABSTRACT

A precise, sensitive and selective spectrophotometric method for determination of aluminium using eriochrome cyanine R (ECR) as a chromogenic reagent in the presence of *N,N* dodecyl trimethylammonium bromide (DTAB) was developed. The Al-ECR complex at pH 5 gave an maximum absorption at 584 nm. The effective parameters of the experimental conditions such as type and amount of surfactant, pH and concentration of ECR were investigated. In the optimized condition of the method presented a linear range of 0.01 – 0.50 mg L<sup>-1</sup> aluminium. The limits of detection and quantification were 0.0020 and 0.0126 mg L<sup>-1</sup>, respectively. The relative standard deviation of the method was 1.3 % (at 0.05 mg L<sup>-1</sup>; n=11). The proposed method was successfully applied for determination of aluminium content in water samples and soft drinks. The results agreed well with those obtained from the ICP-AES method. The good recoveries between 86-106% were obtained.

**Keywords:** Aluminium, Spectrophotometry, Eriochrome cyanine R, Water, Soft drink

*\*Corresponding author*



## INTRODUCTION

Aluminium (Al) is widespread throughout nature, air, water, plants and consequently in all the food chain [1]. Food is the main source of aluminium intake for human body [2]. One of the possible routes through which Al can enter human body could be foods packed in Al containers, e.g. Al cans [3].

Several analytical techniques such as flame atomic absorption spectrometry (FAAS) [4], electrothermal atomic absorption spectrometry (ETAAS) [1,5] and inductively coupled plasma-optical emission spectrometry (ICP-OES) [6-7] devoted to low-level metals determination, however, their present very high acquisition and operational costs. Spectrophotometry is a well-established analytical technique that provides low cost, simplicity and wide range of applications for aluminium determination in some food samples [8-10].

Eriochrome cyanine R (ECR) has been used for the spectrophotometric determination of aluminium in waters [11-12], soils [12], plant tissues [13], hemodialysis [14] and anti-perspirants [15].

In this work, a spectrophotometric method was developed for determination of aluminium content in bottled drinking water, bottled mineral water, tap water, soda and soft drink samples. Eriochromecyanine R (ECR), the most commonly used reagent for Al determination, was proposed as complexing agent in the presence of *N,N*-dodecyltrimethylammonium bromide (DTAB) as cationic surfactant.

## MATERIALS AND METHODS

### Apparatus

Absorbance measurements were carried out with a UV-Vis spectrophotometer (Lamda 25, PerkinElmer Instrument, USA). All pH measurements were made using pH meter (Model 713, Metrohm, Switzerland). ICP-AES (Optima 4300 DV, Perkins Elmer, USA) measurements were carried out as standard method for detection of aluminium concentration at wavelength of 396.153 nm.

### Reagents

All chemicals used were of analytical reagent grade. Deionized water (DI) (obtained from a system of Milli-Q, Millipore, Sweden) was used throughout. A 1000 mg L<sup>-1</sup> Al standard solution (BDH, Belgium) was used through all the experimental work. Working standard solutions of Al with different concentrations were prepared by appropriate diluting the stock solution. A 5 mmol L<sup>-1</sup> eriochrome cyanine R (ECR) stock solution (Merck, Germany) was prepared by dissolving 0.6704 g of ECR in DI water and makes a final volume of 250 mL in volumetric flask. All surfactants including sodium dodecyl sulphate (SDS), Triton X-100, cetyltrimethylammonium bromide (CTAB), *N,N*-dodecyltrimethylammonium bromide (DTAB) were prepared by dissolving appropriate amount of each surfactant in DI water and make a final volume of 50 mL in volumetric flask. Nitric acid (HNO<sub>3</sub>, 70%)



(UNIVAR, Australia) was used for digestion of samples. The 1 mol L<sup>-1</sup> acetate buffer solutions at different pH were prepared from sodium acetate (Carlo Erba, Italy) and acetic acid (Carlo Erba, Italy).

### Sample preparation

Tap water samples were collected in a clean polyethylene bottles (1 L) from the water supply network at different locations in Maha Sarakham Province, Thailand. A total of 18 most frequently consumed brands of water and carbonated beverage samples (including bottled drinking waters, bottled mineral waters, soda drinks and soft drinks) were selected and bought directly from local superstores in Maha Sarakham Province, Thailand. All of samples were produced in Thailand. Each sample consisted of 6 bottles or cans chosen at random which were homogenized immediately before the use.

Tap waters, bottled drinking waters and bottled mineral waters were preserved to pH ≤ 2 by the addition of 2 mL of conc. nitric acid per litre. Soda drink samples were degassed by sonication in an ultrasonic bath for 60 minutes in order to remove CO<sub>2</sub>. No sample pretreatment was made except filtering of the sample just before the analysis.

Soft drink samples were digested by dry-ashing to completely destroy the organic matter. The 10 mL of each soft drink samples were pipetted into porcelain crucibles and the volume was reduced using a hot-plate. Some conc. nitric acid was added and the samples were evaporated until dryness. Finally, the samples were burned in a muffle furnace for 24 h/350 °C. The white ashes were dissolved in 1 mL of conc. nitric acid and transferred to 25 mL volumetric flask, then made up the volume with DI water. After that, samples were transferred into polyethylene bottles and stored at 4 °C until further analysis.

### Spectrophotometric determination of aluminium

Amount of Al in all of real samples was found by standard addition method. In order to build up analytical curves, an appropriate amount of each sample was added to different 25 mL volumetric flasks. To each flask, 1.5 mL of 0.4 mmol L<sup>-1</sup> ECR, 0.5 mL of 1 mmol L<sup>-1</sup> DTAB and 5 mL of 1 mol L<sup>-1</sup> acetate buffer pH 5 and a known volume of a 10 mg L<sup>-1</sup> Al solution were added, in the sequence. After this, the obtained mixture was shaken in order to promote reaction and the volume was completed to the mark with DI water. The absorbance of the final solution was measured at 584 nm against a blank solution containing only the reagents.

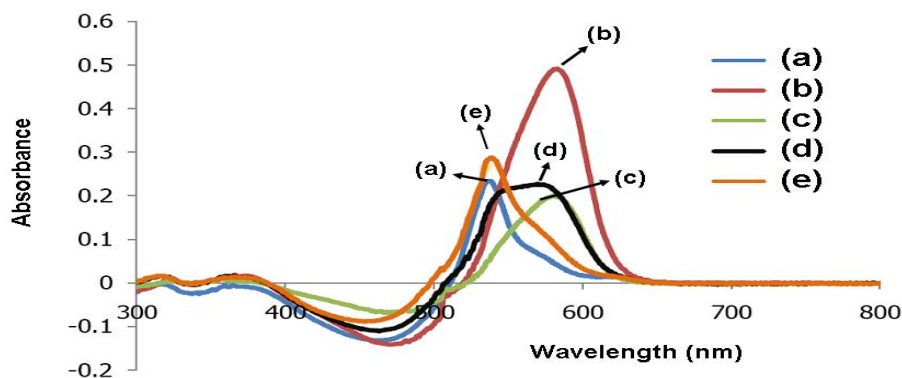
## RESULTS AND DISCUSSION

### Effect of surfactant on sensitivity

The formation of Al-ECR complexes are time consuming, requires rigid control of pH and temperature, and its sensitivity is not suitable for aluminium determination at trace levels. However, these disadvantages can be reduced by applying the cationic surfactant micelles to Al-ECR complex [11,14]. Therefore, the effect of type of surfactant such as cationic (DTAB and CTAB), anionic (SDS) and nonionic (Triton X-100) surfactants on spectra

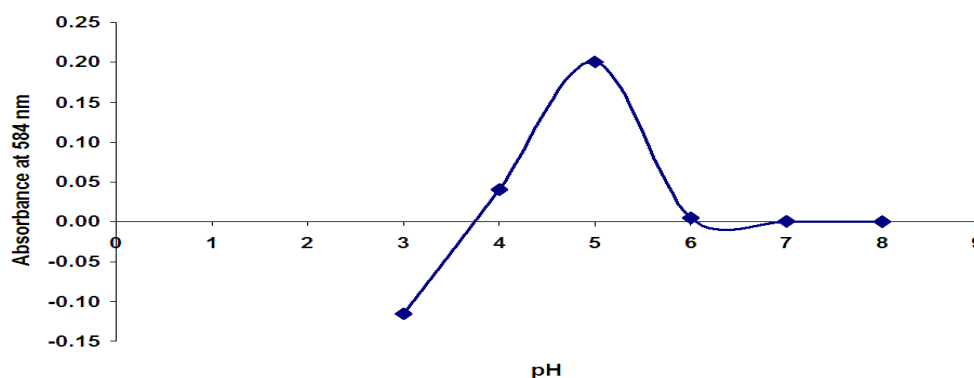
and sensitivity of the complexation of Al and ECR reagent in acetate buffer pH 5 were investigated. It was found that the absorption spectrum of Al-ECR in the presence of DTAB gave highest sensitivity and red shift to maximum wavelength of 584 nm (Fig. 1). Therefore, DTAB was chosen as suitable surfactant for enhances the sensitivity of Al-ECR.

**Figure 1: Spectra of Al-ECR complexes in the absence (a) and in the presence of various surfactants (b) DTAB, (c) CTAB, (d) SDS and (e) Triton X-100. Conditions: 0.2 mg L<sup>-1</sup> Al, 0.15 mmol L<sup>-1</sup> ECR and 3 mmol L<sup>-1</sup> surfactant, pH 5**



### Effect of pH

The pH of the reaction medium was investigated at 584 nm by measuring the absorbance of Al-ECR complex in the presence of DTAB on the pH range of 3-6 using 1 mol L<sup>-1</sup> of acetate buffer. The results indicate that the maximum absorption was obtained at pH 5. Thus, 1 mol L<sup>-1</sup> acetate buffer pH 5 was selected as optimum condition.



**Figure 2: Effect of pH on the absorbance of Al-ECR complex in the presence of DTAB. Conditions: 0.2 mg L<sup>-1</sup> Al, 0.15 mmol L<sup>-1</sup> ECR and 3 mmol L<sup>-1</sup> DTAB.**

### Effect of ECR concentration

The concentration of ECR reagent in range of 0.05-0.5 mmol L<sup>-1</sup> was studied. As can be seen in Fig. 3, increasing the ECR reagent concentration from 0.05-0.4 mmol L<sup>-1</sup>, the absorbance of the Al-ECR complex was increased and then remained constant after the concentration of 0.4 mmol L<sup>-1</sup> ECR reagent was used. Therefore, the concentration of 0.4 mmol L<sup>-1</sup> was chosen from its high sensitivity and high precision.

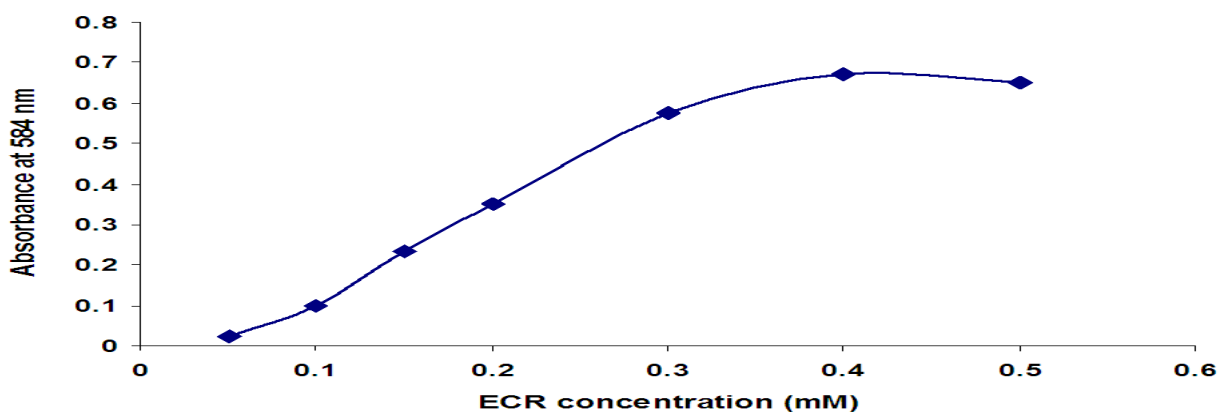


Figure 3: Effect of ECR concentration on sensitivity. Conditions: 0.2 mg L<sup>-1</sup> Al and 3 mmol L<sup>-1</sup> DTAB, pH 5.

### Effect of DTAB concentration

The various concentration of DTAB in the range of 0.1-4 mmol L<sup>-1</sup> was studied for their affect on the absorbance of Al-ECR complex. As presented in Fig. 4, increasing the DTAB concentration from 0.1-0.5 mmol L<sup>-1</sup>, the peak height of the Al-ECR complex was increased and then remained constant for 0.5-1.0 mmol L<sup>-1</sup> DTAB and signal was decreased when the concentration of 2.0-4.0 mmol L<sup>-1</sup> DTAB was used. Therefore, the concentration of 1 mmol L<sup>-1</sup> was chosen from its high sensitivity.

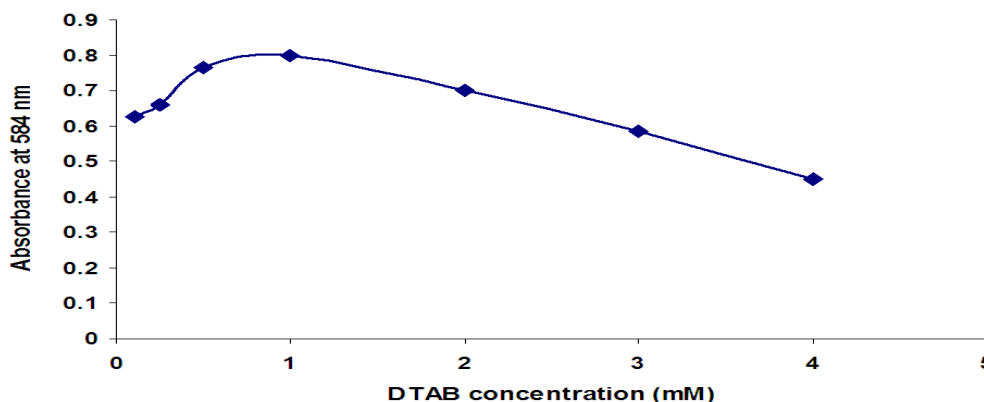


Figure 4: Effect of DTAB concentration on sensitivity. Conditions: 0.2 mg L<sup>-1</sup> Al and 0.4 mmol L<sup>-1</sup> ECR, pH 5.

### Analytical characteristics

Under the selected conditions, the standard calibration of Al in the range of 0.01-0.50 mg L<sup>-1</sup> were constructed by plotting of absorbance versus concentration of Al as presented in Fig. 5. A linear calibration graph could be obtained with the calibration equation  $y = 3.263x + 0.0081$ ,  $R^2 = 0.9986$ . The limits of detection ( $3\sigma/s$ ) and quantification ( $10\sigma/s$ ) (where  $\sigma$  is standard deviation of reagent blank ( $n=11$ ) and  $s$  is the slope of calibration curve) for Al were obtained at 0.0020 and 0.0126 mg L<sup>-1</sup>, respectively. The relative standard deviations for eleven replicate determinations of 0.05 and 0.1 mg L<sup>-1</sup> were 1.3 %, respectively

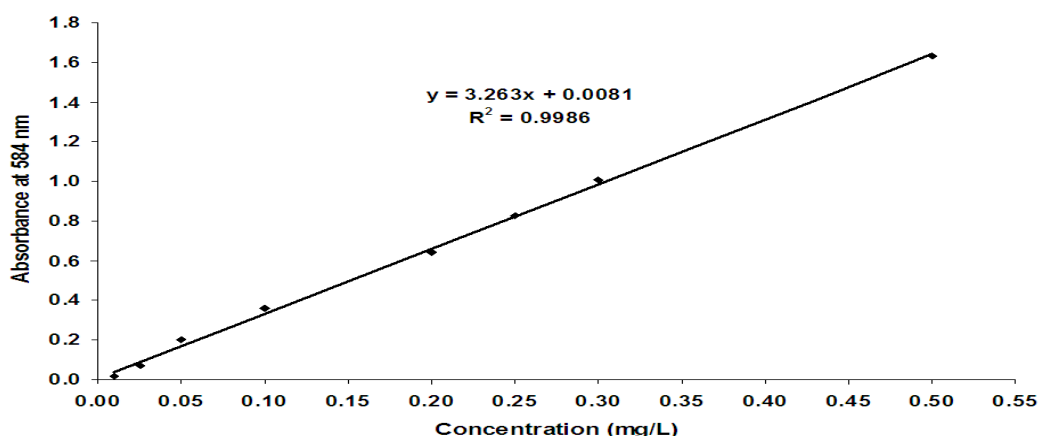


Figure 5: Calibration curve of Al-ECR complexes in the presence of DTAB

### Effect of Foreign ions

The effect of the interfering species upon the Al-ECR-DTAB complex was investigated by the use of the proposed method at optimum conditions. Various concentrations of foreign ions were spiked into a standard solution of 0.2 mg L<sup>-1</sup> Al. Interfering concentration was considered as the concentration that cause signal variation higher than  $\pm 5\%$ . The tolerance limits of interference-to-analyte ratio for some interfering ions are as follow: Na<sup>+</sup> (500:1), Ca<sup>2+</sup> (200:1), Mg<sup>2+</sup> (350:1), Zn<sup>2+</sup> (550:1), Cu<sup>2+</sup> (75:1) and Fe<sup>3+</sup> (1:1). It was found that Fe<sup>3+</sup> and Cu<sup>2+</sup> are major interferences. However, the interfering ions may be effectively eliminated by the addition of ascorbic acid and L-histidine to the measuring solutions [11]. After adding of ascorbic acid and L-histidine, the tolerance limit for Fe and Cu could be tolerated up to 200 fold.

### Application to real samples

The proposed system was employed for determination of aluminium in bottled drinking water, bottled mineral water, tap water, soda and soft drink samples. Some samples were also analyzed by the ICP-AES method for comparison. The obtained results are presented in Table 1. According to  $t$ -test at 95% confident limit, the results obtained from both methods were in good agreement ( $t_{critical} = 2.23$ ,  $t_{calculate} = -0.28$ ). The results were correlated each other well (Spectrophotometry = 0.8757 ICP + 0.039,  $R^2 = 0.9818$ ). The

satisfactory recoveries in range of 86-106% for all samples were obtained, by spiking 0.05-0.2 mg L<sup>-1</sup> of aluminium into samples.

**Table 1: Concentration of aluminium in water and soft drink samples found by spectrophotometric method and ICP-AES**

No.	Type of sample	Sample code	Concentration of aluminium found (mg/L)		% Recovery
			Proposed method (Spectrometry)	ICP-AES	
1	Bottled drinking water	BW1	0.054 ± 0.003	0.060 ± 0.011	98
2		BW2	0.068 ± 0.002	-	104
3	Bottled mineral water	MW1	0.076 ± 0.005	-	103
4		MW2	0.072 ± 0.004	-	98
5		MW3	0.068 ± 0.003	-	101
6		MW4	0.076 ± 0.001	-	106
7	Tap water	TW1	0.289 ± 0.004	0.287 ± 0.018	98
8		TW2	0.311 ± 0.002	0.304 ± 0.005	97
9	Soda	S1	0.082 ± 0.002	-	93
10		S2	0.084 ± 0.005	-	94
11		S3	0.075 ± 0.004	-	106
12		S4	0.073 ± 0.001	-	102
13	Soft drink	SD1	0.141 ± 0.009	0.141 ± 0.035	86
14		SD2	0.183 ± 0.011	0.160 ± 0.006	90
15		SD3	0.208 ± 0.015	0.152 ± 0.016	94
16		SD4	0.703 ± 0.007	0.740 ± 0.009	90
17		SD5	0.229 ± 0.022	0.199 ± 0.012	90
18		SD6	0.395 ± 0.002	0.442 ± 0.011	88
19		SD7	0.222 ± 0.009	0.174 ± 0.012	87
20		SD8	0.482 ± 0.006	0.525 ± 0.012	92

### CONCLUSION

The spectrophotometric method based on complexation of aluminium with eriochromecyanine R in the presence of cationic surfactant was developed. The developed method provides high sensitivity, precision and accuracy. The proposed method was successfully applied with satisfactory results comparing to ICP-AES method for determination of aluminium in water and soft drink samples.

### ACKNOWLEDGEMENTS

The authors are grateful for the financial support from Mahasarakham University Budget fiscal year 2012. The authors wish to thank Yaowalak Khanhuathon, Lakkhana Tornonsung and Sukanya Chomputorn for the assistance of this work.

### REFERENCES

- [1] Lopez FF, Cabrera C, Lorenzo ML, Lopez MC. Sci Total Environ 2002; 292: 205-213.
- [2] Soni MG, White SM, Flamm WG, Burdock GA. Regul Toxicol Pharm 2001; 33: 66-79.
- [3] Seruga M, Grgic J, Mandic M. Z Lebensm Unters For 1994; 198: 313-316.
- [4] Neelam, Bamji MS, Kaladhar M. Food Chem 2000; 70: 57-61.



- [5] Jalbani N, Kazi TG, Jamali MK, Arain BM, Afridi HI, Baloch A. *J Food Compos Anal* 2007; 20: 226-231.
- [6] Malik J, Frankova A, Drabek O, Szakova J, Ash C, Kokoska L. *Food Chem* 2013; 139: 728-734.
- [7] Scancar J, Stibilj V, Milacic R. *Food Chem* 2004; 85: 151-157.
- [8] Francisco BBA, Caldas LFS, Brum DM, Cassella RJ. *J Hazard Mater* 2010; 181: 485-490.
- [9] Abbasi S, Farmany A, Gholivand MB, Naghipour A, Abbasi F, Khani H. *Food Chem* 2009; 116: 1019-1023.
- [10] Tontrong S, Khonyoung S, Jakmunee J. *Food Chem* 2012; 132: 624-629.
- [11] Shokrollahi A, Ghaedi M, Niband MS, Rajabi HR. *J Hazard Mater* 2008; 151: 642-648.
- [12] Luo M, Bi S. *J Inorg Biochem* 2003; 97: 173-178.
- [13] Honorato RS, Carneiro JMT, Zagatto EAG. *Anal Chim Acta* 2001; 441: 309-315.
- [14] Rodrigues JL, de Magalhaes CS, Luccas PO. *J Pharm Biomed Anal* 2005; 36: 1119-1123.
- [15] Lopez-Gonzalvez A, Ruiz MA, Barbas C. *J Pharm Biomed Anal* 2008; 48: 340-346.