The Analysis of Al^{3+} via Liquid-Liquid Extraction by Curcumin in the Presence of Picric Acid

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Abstract: *This study reported on the proposed analysis of aluminium (Al) via solvent extraction by curcumin (Cur) in the presence of picric acid (Pic) using UV-visible spectrophotometry method. The 1:2 molar ratio of Al:Cur was obtained in methyl isobutyl ketone (MIBK) and in phosphate buffer (pH 9.00). The resulting complex had its maximum absorption peak at 378 nm instead of at 420 nm for Cur. The Fourier-transform infrared (FTIR) spectrum proved that Pic was not in the complex structural formation, but instead acted as its counter ion. Preliminary results on the analysis of Al^{3+} in selected canned food samples have indicated that they were comparable to a standard method.*

Keywords: aluminium, curcumin, picric acid, solvent extraction

Abstrak: *Kajian ini melaporkan cadangan analisis aluminium (Al) melalui pengekstrakan pelarut oleh kurkumin (Cur) dengan kehadiran asid pikrik (Pic) menggunakan kaedah spektrometri UV-nampak. Nisbah mol 1:2 terhadap Al:Cur telah diperoleh dalam metil isobutil keton (MIBK) dan dalam penimbal fosfat (pH 9.00). Kompleks yang dihasilkan mempunyai puncak keserapan maksimum pada 378 nm berbanding 420 nm bagi Cur. Spektrum FTIR membuktikan bahawasanya Pic tidak terlibat dalam struktur kompleks sebaliknya sebagai ion lawan. Keputusan awal terhadap analisis Al^{3+} dalam sampel makanan dalam tin terpilih menunjukkan ianya standing dengan kaedah piawai.*

Kata kunci: aluminium, kurkumin, asid pikrik, pengekstrakan pelarut

1. INTRODUCTION

Aluminium is the second most abundant metal in the earth crust next to iron. It is widely used in industrial applications as well as in domestic uses. Indirect intake of Al^{3+} into our body cannot be ignored as the accumulation of Al^{3+} in brain has been identified to cause diseases such as Alzheimer.[1] Thus, the analysis of aluminium, especially in food samples is very critical.

Al^{3+} is usually difficult to analyse as it is susceptible to hydrolysis by forming $Al(OH)_4^-$, usually at a higher pH.[2] At higher temperature such as in flame, it easily forms aluminium oxide, a refractory compound resisting

decomposition during atomic spectrometry. It is equally difficult to be reduced directly at mercury (Hg) electrode, but only feasible through complex formation with suitable ligand prior to reduction.[3] Still, the complexation reaction needs at least an hour to complete. Because of this, the molecular fluorescence method making use of ligand 8-hydroxyquinoline in chloroform has been used as the preferred method for the analysis of Al^{3+}.[4] However, this method is now prohibited partly due to the hazardous solvent used and the susceptibility of the method to physico-chemical conditions. To date, the UV-visible spectrophotometry of Al^{3+} using ligand chromoazurol S is the only suitable technique.[5]

Curcumin (Cur), a natural colorant, non-toxic ligand and antioxidant, has been known as an excellent reagent for the analysis of boron (B),[6] an element in similar group as is Al. Since the formation of Al-Cur have been reported[7,8] and also preservative effect of Cur in pickle brine in the presence of Al^{3+} is more pronounced,[9] the interest to exploit Cur in the analysis of Al^{3+} began to be reported recently.[10] However, the study has many flaws and dubious results; for example λ_{max} for Cur at 550 nm is similar to one for Al-Cur. Hence, it is almost impossible to decide which absorbance is which. Thus, this will affect the quantity of Al^{3+} measured. The complex formation at the optimum pH 11.3 is absurd as at this pH, Al^{3+} is more favorable of forming Al(OH)$_4^-$,[2] than to form Al-Cur. Finally, the molar ratio of Cur:Al at 1:2 is unimaginable as stereochemically, this is not allowed. Thus, this study is aimed at proposing a similar approach, i.e., using Cur as primary ligand but with the addition of a suitable secondary ligand for a more effective way of analysing Al^{3+}.

2.   EXPERIMENTAL

2.1   Reagents and Chemicals

All analytical grade salts and ligands were supplied either by Sigma Chemicals, USA or Fluka Chemie, Switzerland and were used as obtained. Buffer tris-(hydroxyl methyl) amino methane hydrochloride or Tris-HCl was supplied by Sigma Chemicals, USA. Most surfactants were purchased from Sigma Chemicals, USA except Decon 90® (Decon Lab., UK) and 10% (w/v) Triton X-100 (Boehringer Mannheim, Germany). The standard Al solution was prepared by dissolving Al casting alloy 380 of Standard Reference Material 856a (NIST, Maryland, USA) in hot 6 M nitric acid before dilution. The phosphate buffer (pH 9.00) was a mixture of 0.2 M KH$_2$PO$_4$, 0.2 M Na$_2$HPO$_4$ and 0.3 M Na$_3$PO$_4$. Water (18.2 MΩcm) for dilution was from either Direct-Q3 or Milli-Q Plus (Millipore, USA).

2.2   Instrumentations

The UV-visible spectrophotometer model V530 (JASCO, Japan) was used for absorbance measurements. The Fourier-transform infrared (FTIR) spectrophotometer model 200 (Perkin Elmer, USA) was used for structural analysis. The atomic absorption spectrophotometer model 3100 (Perkin Elmer, USA) was used to determine Al in aqueous phase. The pH measurements were performed using pH meter model 520A c/w pH electrode model 915600B (Orion Research Inc, USA). The programmed mechanical shaker (Stuart Scientific, UK) was used for the equilibration/agitation of organic and aqueous phases.

2.3   Procedure

A 1.0 mL Al solution was placed in a small beaker. Five drops of 0.1 M sodium tartrate were added to inhibit the formation of insoluble Al.[11] The pH of the mixture was adjusted to 9.00 by adding buffer solution. The aliquot was then diluted to a total volume of 10 mL. The final solution was transferred into a 100 mL separating funnel, after which 10 mL of 1×10^{-6} M Cur in MIBK and 2 mL of 2×10^{-6} M Pic were added. The mixture was agitated for 5 min at $25 \pm 5^{\circ}$C after which 30 min separation was given for the organic layer to be separated nicely from the aqueous. The organic layer was then measured for its absorbance at 378 nm. The proposed method was validated against the reference chromoazurol S method.[5]

3.   RESULTS AND DISCUSSION

Figure 1 shows λ_{max} of Al-Cur and Cur in MIBK overlapping each other at 420 nm. Additional secondary ligands in excess, including oxalate which has been used in the complexation of B and Cur,[6] have not shifted the λ_{max} of Al-Cur except when picric acid (Pic) was used (Table 1). A hypsochrome or blue shift to 378 nm is noticeable when Pic was added (Figure 1). It is also interesting to note that the absorption peaks of Al-Cur and Al-Pic and their respective ligands appear to have overlapped each other, making it difficult to access the extend of the complexations. In case of Al-Pic, there might be no complex at all as there is no enhancement of absorption peak. Further to this, the mixture of Cur and Pic tends to produce its own absorption peak indicating presence of reaction between both. However, a more intense absorbance has been displayed as Al^{3+} is added into the mixture producing no overlapping whatsoever with absorption peak of other compositions available [Figure 1(f)].
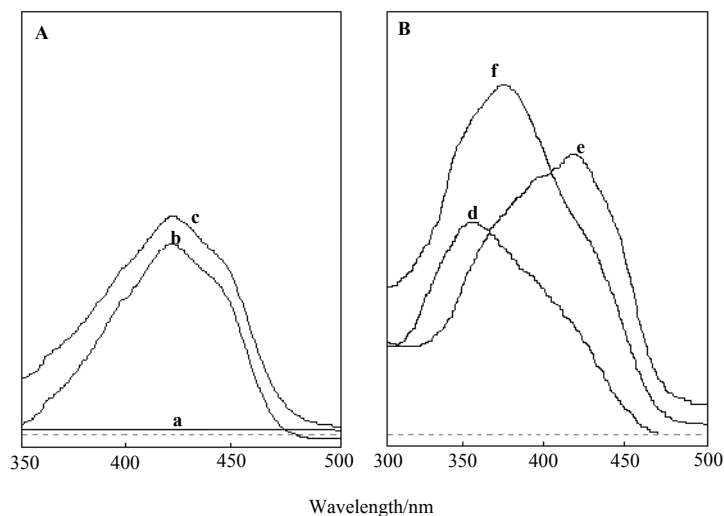
Figure 1: The UV-visible spectra of organic phase (in MIBK) of (a) 1×10^{-6} M Al^{3+} in aqueous; (b) 2×10^{-6} M Cur; (c) 1×10^{-6} M Al^{3+} and 2×10^{-6} M Cur; (d) 1×10^{-6} M Al^{3+} and 2×10^{-6} M Pic and 2×10^{-6} M Pic only; (e) 2×10^{-6} M Cur and 2×10^{-6} M Pic ; (f) 2×10^{-6} M Cur, 1×10^{-6} M Al^{3+} and 2×10^{-6} M Pic.

Pic has been utilised as secondary ligands in other liquid-liquid extraction systems.[12,13] It is only coincidental that this study happens to have the same benefit from Pic (Table 1). However, this study is more interested on the application of Cur as ligand in the analysis of Al^{3+}. But, it is also worthwhile to check on the function of Pic that causes the blue shift for Al-Cur. Pic is only slightly soluble in water ($pK_a = 0.38$) but very soluble in ketone.[14] Thus, during 5 min agitation of the phases, Al, a hard acid,[15] in aqueous should have reacted with Pic, a hard base, in MIBK prior to reaction with Cur, a soft base. However, Figure 1(d) indicates that there might be no such reaction. Figure 2 demonstrates that as $[Al^{3+}]$ and [Cur] remain constant, the absorbance at 378 nm increases with increase in [Pic]. This shows that Pic in excess is vital for the formation of a stable complex useful for the analysis of Al. By using equation of log D = log K + n pH,[16] this extraction system (in equilibrium) has at least two moles of each primary and secondary ligands involved in the reaction as well as two moles of proton liberated.

Table 1: The λ_{max} of Al-Cur in presence of secondary ligands.

Secondary Ligands	λ_{max} (nm)
L-ascorbic acid	419.00
monosodium Azomethin-H hydrated	420.00
2,2'-Bipyridyl*	420.00
Catechol violet	421.00
Citric acid	419.00
3,5-dichloro-2-hydroxy-benzenesulfonic acid	421.00
β-cyclodextrin	420.00
di-Sodium ethylene diamine tetraacetate	421.00
3-hydroxy-2-naphthoic acid*	420.00
Hydroxylamine hydrochloride	421.00
N,N,N,N'-Tetra-methylethylenediamine	421.00
o-phenanthroline*	421.00
Oxalic acid	421.00
Picric acid	378.00
ammonium 1-pyrrolidinedithio-carboxylate*	420.00
Sodium diethyl-dithiocarbamate*	421.00
Tetramethyl ammonium chloride	420.00

*sparingly soluble
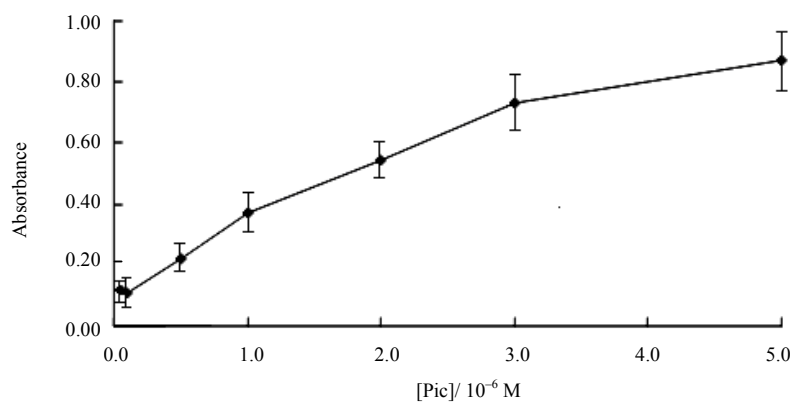
Figure 2: The effect of Pic concentrations on the formation of Al-Cur. The concentrations of Al^{3+} and Cur remain constant at 1×10^{-6} M and 2×10^{-6} M, respectively (n = 3).

The molar ratio of a Metal-Cur complex depends on the Metal, Cur and other chemical species in the system.[6,7,17] From Job's plot and with [Pic] remains constant, the molar ratio of Al:Cur of 1:2 is obtained (Figure 3). The calculated stability constant (K) of 1.54×10^{12} indicates that Al-Cur formed is relatively a stable complex. The two moles Cur taking part in the formation of Al-Cur justifies the liberation of two H$^+$ mentioned earlier. As Cur species are very much pH dependent, at pH 9.00 the dominant species have always been the enolate.[6,17] At this pH, the liberated H$^+$ is presumably neutralised by the OH$^-$ from the coordination sphere of Al.[18] Even though most chelates of β-diketone are formed in acidic media,[19] beryllium (Be) which has "diagonal relationship"[20] with Al in periodic table has formed complex with Cur in a more basic condition i.e., at pH 10.00.[21] In that respect, it is also likely that Al-Cur has formed at pH 9.00.
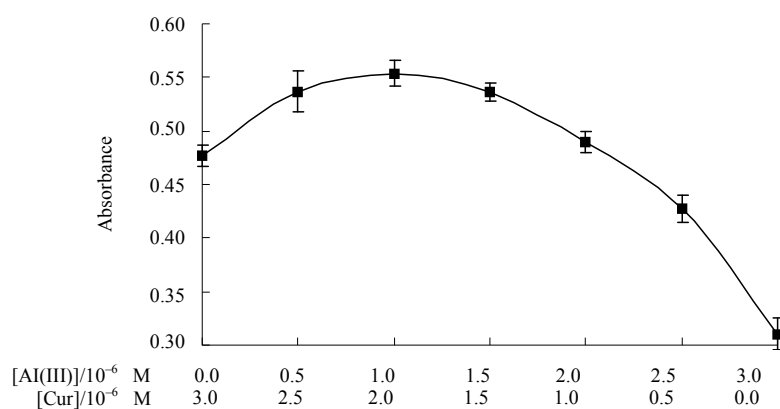

Figure 3:   The Jobs plot of Al-Cur at λ_{max} 378 nm. The concentration of Pic solution remains at 2×10^{-6} M (n = 3).

In Figure 4, the FTIR spectrum shows that the $\mathbf{v_{C=O}}$ stretching band (1640–1750 cm^{-1}) in Cur appears at a lower wave number, 1510 cm^{-1}. This might be attributed to the intra molecular hydrogen bonding between carbonyl and hydroxyl in the keto-enol. At this wave number, Al-Cur appears to have indistinctive absorption which indicates the coordination of Al and Cur. The band has shifted to a higher wave number at 1720 cm^{-1} as the complex is formed. This shows the new addition of carbonyl at the phenolic group. Similarly, Al-Cur shows no absorption band at 3103 cm^{-1} which characterises the weak OH band of picric acid. Instead, this $\mathbf{v_{OH}}$ stretching band has shifted to lower wave number 3325 cm^{-1}. This may indicate that Pic exists as the counter ion or ion pair in the complex formed. However, the strong $\mathbf{v_{OH}}$ stretching band of Cur in the complex at 3600 cm^{-1} has also disappeared. Thus, the decrease in $\mathbf{v_{C-OH}}$ stretching band further support Al binds to Cur at the enol group. Additionally, the presence of

Pic in the overall reaction could be as a proton mediator—to shuttle protons from the organic phase to the aqueous phase to promote complex formation. Hence, the absorbing species at λ_{max} 378 nm would be the cationic complex $[Al(Cur)_2]^+$ in paired with counter ion Pic$^-$. The whole mechanism of reaction for the extraction system is then proposed as shown in Figure 5.
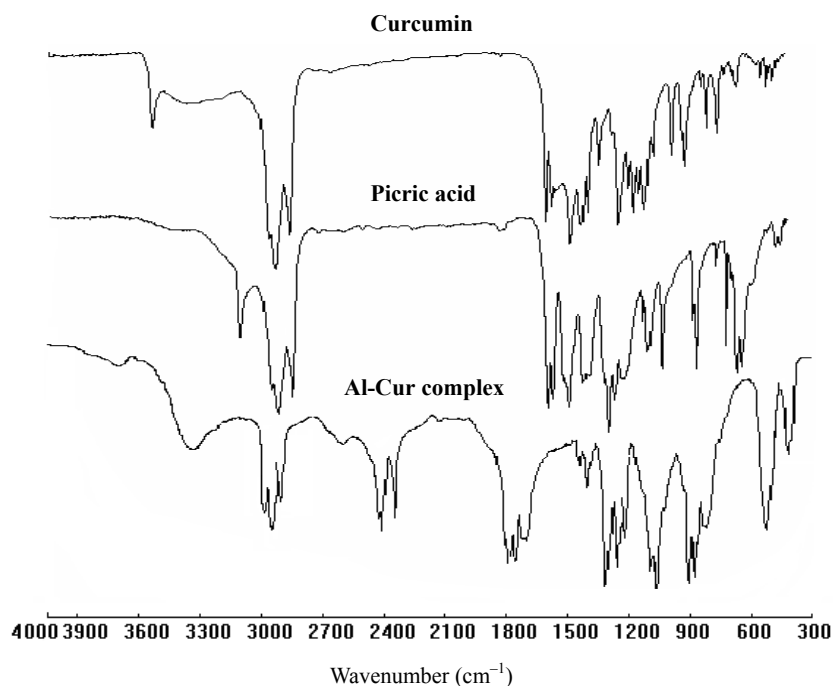

Figure 4: The FT-IR spectra of Cur, Pic and Al-Cur complex in the presence of picric acid in MIBK.

Of all the conventional (for solvent extraction) solvents tested (Table 2) MIBK is the most suitable for Cur and also its complex. This like–dissolves-like ketone produces the largest molar extinction coefficient (ε) value for Al-Cur at 9.04×10^4 L mol^{-1} cm^{-1} indicating a relatively sensitive combination obtainable out of the UV-vis spectrophotometry used. The compatibility of solvent and solute is also demonstrated in the percentage of extraction (E) of Al-Cur from a single extraction at optimum pH 9.00 (phosphate buffer) and in the order of MIBK (86%) > 1,2-dichloroethane ≈ dichloromethane (62%) > isoamyl alcohol (53%) > toluene (48%). The non-extracted Al in aqueous phase is determined by atomic absorption spectrometry and is later collected either by subsequent extraction or back extraction. Additional of some generally known salting-out agents and surfactants do not increase E. The optimum pH at 9.00 indicates that

buffering by phosphate system is preferred. This is more convenient and better than reference methods which use acids and bases solutions.

Table 2: The absorbances of Cur and Al-Cur in various solvents at pH 9.00.

| Solvents	Cur solubility	Cur (λ_{max}/ nm)	Abs.	Al-Cur (λ_{max}/ nm)	Abs.
iso-amyl alcohol	soluble	430.0	0.2168	363.0	0.6656
iso-butyl alcohol	soluble	430.0	0.1710	357.0	0.7565
Dichloromethane	soluble	417.0	0.1759	356.0	0.6890
Tetrachloromethane	sp. soluble[*]	412.0	0.2550	356.0	0.6920
Diethylether	soluble	415.0	0.2298	416.0	0.2770
Toluene	soluble	417.0	0.1840	417.0	0.1746
1,2-Dichloroethane	soluble	417.0	0.3741	356.0	0.7044
MIBK	soluble	420.0	0.2200	378.0	0.8231
Benzene	soluble	418.0	0.3391	418.0	0.3694
Hexan-1-ol	soluble	430.0	0.1912	360.0	0.6696
Cyclohexane	insoluble	-	-	-	-
n-Hexane	insoluble	-	-	-	-

[*] sp. denotes sparingly
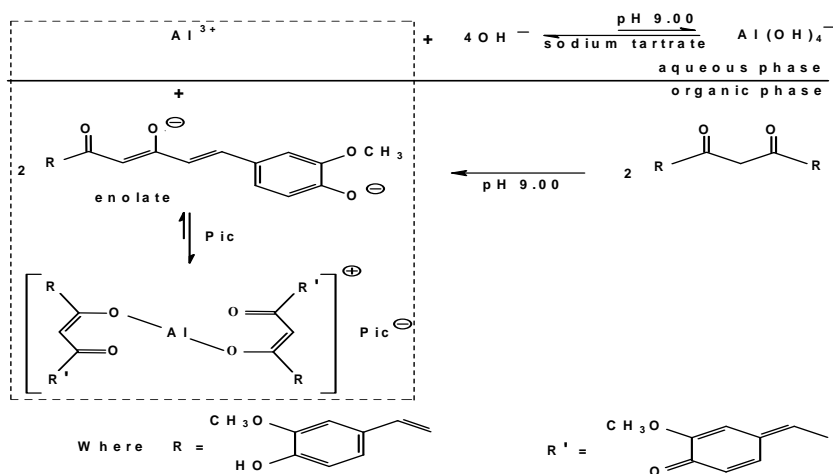
Figure 5: Schematic representation of liquid-liquid extraction of Al^{3+} as Al-Cur in the presence of Pic in MIBK.

From the calibration plot, the absorbance is found to be linearly (y = 0.090x + 0.466) dependent on the Al-Cur concentration ranges up to 3.0×10^{-5} M Al^{3+} with limit of detection (LOD) at 4.8×10^{-8} M Al^{3+} (S/N = 3). The chromoazurol S method, however, has a linearity up to 1.0×10^{-5} M Al^{3+} and LOD at 2.2×10^{-7} M Al^{3+}. A good correlation (R^2 = 0.9874) and insignificant difference [t-test (P > 0.05)] are obtained between both methods.

The interferences from cations usually compete with Al for ligands have been studied (Figure 6). It shows that with the additional of 2×10^{-5} M to 1×10^{-4} M of the cations, the absorbances of the complex have decreased in the order of $Fe^{3+} > Ga^{2+} > Mg^{2+} > Ca^{2+} > Cu^{2+}$. A serious interference from Fe^{3+} would probably jeopardise analysis of Al where dissolved iron (III) is abundant e.g., in environmental waters.
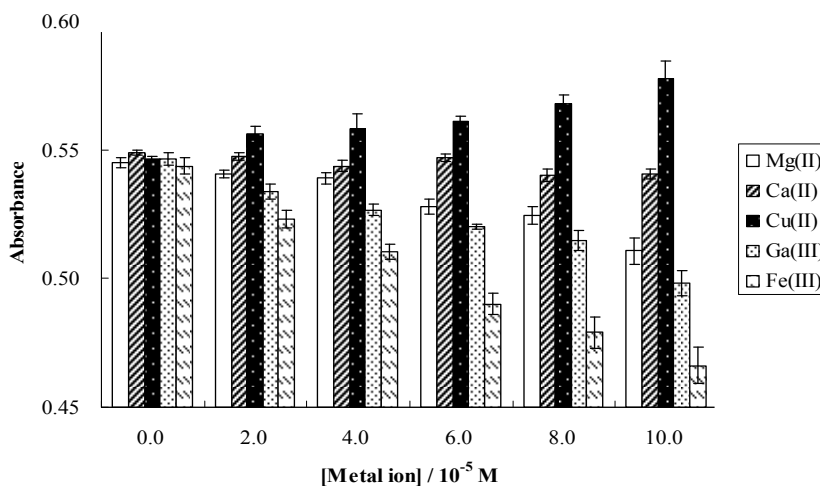

Figure 6: The interferences of other metal ions in the extraction system.

The amount of Al in selected liquid samples, especially in canned food, has been analysed through multiple extractions at optimum parameters (Table 2). The percentage of recoveries (R %) are quite remarkable. Results indicate that there is possibility Al^{3+} has leached out from some of the containers into the liquid it contains. The situation can be even worse in case of food prepared in aluminium pan with white vinegar added in. Regular consumption of food prepared in this way is potentially dangerous as accumulation of Al in brain cells has been blamed for causing Alzheimer.[1] The risk increases through drinking of ground water with Al level at 0.10 to 0.20 μg mL^{-1}.[22]

Table 3:   Analyses of Al in liquid samples through extraction by the proposed and reference methods (n = 3).

Samples	Al (μg mL^{-1})		Al Spiked (μg)	Al Found (μg)		Recovery (%)	
	Chromo azurol S	Curcumin		Chromo azurol S	Curcumin	Chromo azurol S	Curcumin
Tap water	0.55 ± 0.02	0.54 ± 0.02	10.0	9.56 ± 0.05	9.60 ± 0.05	95.6	96.0
Tonic water	0.11 ± 0.01	0.11 ± 0.02	10.0	11.0 ± 0.1	10.5 ± 0.3	110.3	105.0
Soda water	0.43 ± 0.01	0.40 ± 0.01	10.0	10.0 ± 0.1	10.6 ± 0.5	108.0	106.4
Ginger ale	0.21 ± 0.02	0.21 ± 0.02	10.0	9.43 ± 0.05	9.55 ± 0.05	94.3	95.5
Chrysanthemum tea	0.22 ± 0.01	0.22 ± 0.01	10.0	9.87 ± 0.05	10.1 ± 0.1	98.7	101.2
Litchi juice	0.14 ± 0.01	0.17 ± 0.01	10.0	9.62 ± 0.05	9.68 ± 0.05	96.2	96.8
Tomato juice	0.72 ± 0.01	0.70 ± 0.02	10.0	10.5 ± 0.1	10.7 ± 0.1	104.8	106.5
Lemon juice in Al pan	0.21 ± 0.01	0.26 ± 0.02	10.0	9.24 ± 0.05	9.46 ± 0.1	92.4	94.6
Vinegar in Al pan	4.09 ± 0.02	4.09 ± 0.01	10.0	10.1 ± 0.1	9.70 ± 0.05	100.5	97.0

4.   CONCLUSION

This study has demonstrated that Cur, in the presence of Pic can be used as an alternative ligand in the analysis of Al. The quantification of Al is viable as the λ_{max} of Al-Cur (with Pic) is different from those of Cur, Al-Cur (without Pic), Pic and Al-Pic. The presence in excess of Pic is vital because besides acting as counter ion or ion pair for the Al-Cur cationic complex, it also mediates (facilitates) the transfer of proton from Cur prior to complexation. The proposed method (Cur) appears more sensitive and selective than the reference (chromoazurol S).

5.   ACKNOWLEDGEMENTS

6.   REFERENCES

1.   Mclachlan, D. R. C., Bergeron, C., Smith, J. E., Boomer, D. & Rifat, S. L. (1996). Risk for neuropathologically confirmed Alzheimer's disease and residual aluminum in municipal drinking water employing weighted residential histories. *Neurol.*, 46(2), 401–405.

2.   Driscoll, C. T. & Schecher, W. D. (1989). *Aluminum and health – A critical review*. In Gitelman, H. J. (Ed.). New York: Marcel Dekker, 27–65.

3.   Downard, A. J., Powell, J., Kipton, H. & Xu, S. H. (1991). Voltammetric determination of aluminium(III) using a chemically modified electrode. *Ana. Chim. Acta,* 251(1–2), 157–163.

4.   Gentry, C. H. R. & Sherrington, L. G. (1946). The direct photometric determination of aluminum with 8-hydroxyquinoline. *Analyst,* 71(846), 432–443.

5.   Matsushita, T., Kaneda, M. & Shono, T. (1979). Synergic effects of poly(vinylbenzyltriphenylphosphoniumchloride) on the spectrophoto-metric determination of lanthanum, aluminum and beryllium. *Anal. Chim. Acta,* 104(1), 145–151.

6.   Roth, H. J. & Miller, B. (1964). On the color reaction between boric acid and curcumin. II. On the constitution of rosocyanins and rubrocurcumins. *Arch. Pharm.,* 297(11), 660–673.

7.   Maing, Y. & Miller, I. (1981). Curcumin-metal color complexes. U.S. Patent 4,263,333, filed Sept. 12, 1979, issued Apr. 21, 1981.

8.   Yang, L. & Buescher, R. (1993). Dye and method for making same. U.S. Patent 5,210,316, filed Feb. 4, 1991, issued May 11, 1993.

9.   Buescher, R. & Yang, L. (1990). Stabilization of curcumin as a food colorant. *J. Food Biochem.,* 14, 263–271.

10.   Arzigul, I. & Liu, H. (2008). The determination of Al^{3+} in pollution water by spectrophotometic curcumin method. *Xinjiang Yike Daxue Xuebao*, 31, 262–264.

11.   Stary, J. (1964). *The solvent extraction of metal chelate*. New York: Macmillan.

12.   Salleh, M. I., Salhin, A. & Saad, B. (1995). Determination of lanthanum in monazite sand after solvent extraction separation of the picrate with dibenzo-24-crown-8. *Analyst*, 120(12), 2861–2865.

13.   Matus, P., Kubova, J., Bujdos, M. & Medved, J. (2006). Free aluminum extraction from various reference materials and acid soils with relation to plant availability. *Talanta*, 70(5), 996–1005.

14.   Patai, S., Zabicky, J. & Rappoport, Z. (1976). *Handbook of chemistry and physics*, 57th ed. Cleveland: CRC Press.

15.   Pearson, R. G. (1963). Hard and soft acids and bases. *J. Am. Chem. Soc.*, 85(22), 3533–3539.

16.   Morrison, G. H. & Freiser, H. (1966). *Solvent extraction in analytical Chemistry.* New York: John Wiley, 50–59.

17.   Dietze, F., Arrieta, F. & Zimmer, U. (1997). pKa stability constants and UV/VIS spectral behaviour of selected curcumin analogues. *Pharm., 52*(4), 302–306.

18.   Krackov, M. H. & Bellis, H. E. (1997). Process for the synthesis of curcumin-related compounds. U.S. Patent 5,679,864, filed Nov. 3, 1995, issued Oct. 21, 1997.

19.   Stary, J. & Hladky, E. (1963). Systematic study of the solvent extraction of metal β-diketonates. *Anal. Chim. Acta*, 28, 227–235.

20.   Huheey, J. E. (1975). *Inorganic chemistry*. London: Harper & Row, 604–605.

21.   Gao, H. W. & Zhang, P. F. (1996). Pyridine-curcumin spectrophotometric determination of beryllium in industrial wastewater. *Meas. Tech.*, 3, 26–27.

22.   Jaqmin, H., Commenges, D., Lettneur, L., Baberger-Gataeu, P. & Dartigues, J. F. (1994). Components of drinking water and risk of cognitive impairment in the elderly. *Am. J. Epidemiol.*, 139(1), 48–57.