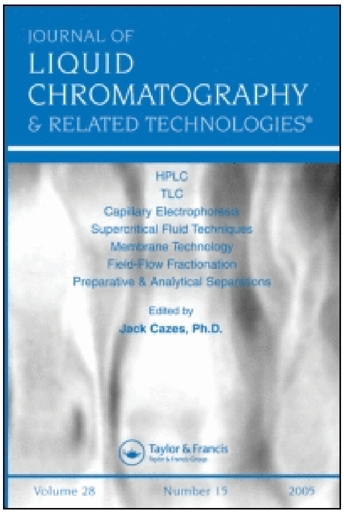

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Extraction with Toluene and HPLC Determination of Aluminum in the Form of an 8-Hydroxyquinoline Derivative

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ABSTRACT

A reversed-phase high performance liquid chromatographic method for determination of trace amounts of aluminum has been developed using 8-hydoxylquinoline (8-HQ) as the precolumn reagent, and low-volatile toluene as the extraction reagent for the first time. The 8-HQ complex of Al was formed in weak basic medium and extracted to toluene. The separation was achieved on a PC8-10 column with the mobile phase of 40 : 40 : 20 methanol : acetyl acetate : 25 mmol/L lithium lactate (pH 8.0) at a flow rate of 1.0 mL/min. Excellent sensitivity was obtained by spectrophotometric detection at 390 nm and the detection limit was

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0.08 ng. The response of Al is linear from 0.04 μg/mL to 1.0 μg/mL with a 10 μL injection. The extraction efficiency and precision of analyses were significantly improved. The proposed method has been successfully applied to the direct determination of Al in drinking and natural waters with the recoveries of 92.7–101.0%.

Key Words: Aluminum; Toluene extraction; 8-hydroxyquinoline derivative.

INTRODUCTION

It is well known that elevated aluminum concentrations in natural waters resulting from acid rain are toxic to aquatic and terrestrial organisms.[1] Recently, the available evidences pointed to the conclusion that uptake of Al by different ways, including drinking waters, might cause serious neurotic diseases, such as Alzheimer's disease, Parkinson's disease, and dialysis encephalopathy.[2] All of these made the determination of Al in drinking and natural waters very important. Because of the low concentrations, research work has been carried out in the last two decades, in developing ultra-sensitive analytical techniques for determining trace levels of Al in such samples. The most commonly used analytical methods are graphite furnace atomic absorption spectrophotometry (GF-AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES). The detection limits of these techniques are about 0.001 μg/mL, but in this range their precision is poor.[3–5]

High performance liquid chromatography (HPLC) has been successfully applied to the determination of Al in the form of various complexes.[6–10] Al-8-HQ should be the only chelate exhibiting rapid reactivity and good chromatographic property.[6,11,12] However, since it had poor performance at low level, 8-HQ was added in the mobile phase in order to prevent decomposition of the chelate.[6,11,13,14] The presence of the ligand in the eluent made the background absorbance increase and then sensitivity decrease. In addition, the column was periodically washed with methanol or acetonitrile for removing accumulation of adsorbed ligand. Extraction of the chelate from aqueous solution to organic solvent can overcome the above described problems, although the procedure was somewhat time-consuming. Chloroform was the most commonly employed extracting solvent for HPLC analysis of Al-8-HQ.[6,15,16] However, it is so volatilizable that the exact quantitation was more difficult to obtain. In the present work, toluene is recommended as the extracting agent instead of chloroform for lower volatility, lower toxicity, better precision, and low cost. The HPLC method with UV-detection, with

8-HQ as precolumn reagent after extraction with toluene, has proven to be applicable to the determination of Al in tap, potable, pond, and river waters.

EXPERIMENTAL

Apparatus and Reagents

The chromatographic system consisted of Shimadzu units LC-6A pump, SPD-6AV UV-VIS spectrophotometric detector, and C-R4A integrator. A Rheodyne 7125 injector was used with a loop volume of 10 μL. A PC8-10 column (10 μm, 250 × 4.0 mm I.D.: Dalian Institute of Chemical Physics, Academia Sinica, Dalian, China) was used throughout.

A Mettler Toledo 320 pH meter equipped with an HA405-K2/120 combination electrode (Mettler-Toledo Instruments Shanghai Co. Ltd, Shanghai, China) is used for pH measurement. All glassware and high-density polyethylene containers are carefully treated with 2 mol/L nitric acid and rinsed several times with twice distilled water.

All solvents and reagents used were of analytical-reagent grade unless otherwise stated. High performance liquid chromatographic -grade methanol is purchased from Tedia Company, Inc. (Fairfield, OH). Water was deionized and twice distilled from a quartz device. Stock standard aluminum solution containing 1000 μg/mL Al was provided by ICP-AES laboratory, Center of Materials Analysis, Nanjing University (CMANU). All working standard Al solutions were prepared by immediate serial dilution. The 8-HQ was purified by recrystallizing from hot ethanol. The 8-HQ solution (2.5 w/v%) was prepared by dissolving 25 g of the compound in 20 mL of 6 mol/L HCl and diluting to 1000 mL with water. The preparation of pure Al-8-HQ precipitate used for the acquisition of extraction efficiency and retention data, in the optimization of chromatographic conditions, was based on the familiar method of Miller and Chalmers [17] and its modification.[18] Toluene used for extraction of Al-8-HQ was purified by distillation. Drinking waters were purchased from a supermarket in Nanjing, tap waters drawn from the local supply system of Nanjing and Nantong, respectively. Natural waters were collected from pond, lake, and river in Nanjing, Yangzhou, and Suinin, respectively.

General Procedure

A 5 mL aliquot of the Al solution was pipetted into a 10 mL comparison tube and the pH was adjusted to 7.5–8.0 by adding about 0.5–1.0 mL 1.0 mol/L Tris(hydroxymethyl)aminomethane (Tris)-HCl (pH 8.0). Then, an over 6-fold molar excess of 8-HQ was added. The solution is sonicated for 5 min. The 8-HQ chelate of Al, such obtained, was once extracted by adding 1.00 mL of toluene. A 10 µL aliquot of the solution was injected into the chromatograph. The mobile phase was a mixture of 40% methanol, 40% ethylacetate, and 20% water containing 25 mmol/L lithium lactate (pH 8.0 with Tris-HCl). Elution was achieved at 1.0 mL/min. The column temperature was 30°C and the detection wavelength 390 nm.

RESULTS AND DISCUSSION

Quantity of 8-HQ and Extraction Efficiency of Al-8-HQ

As shown in Fig. 1, for determining 2.5 µg Al in 5 mL (ca. 0.09 mmol/L) of standard solution, as long as the molar ratio of 8-HQ to Al reached 5 : 1, the peak area of Al-8-HQ was constant under the proposed procedure. Considering the strong molar absorptivity of unreacted ligand at 390 nm, the molar rate should be minimized, not exceeding 500 : 1. The extraction efficiency of Al-8-HQ by toluene was checked by dissolving pure precipitate of the chelate in

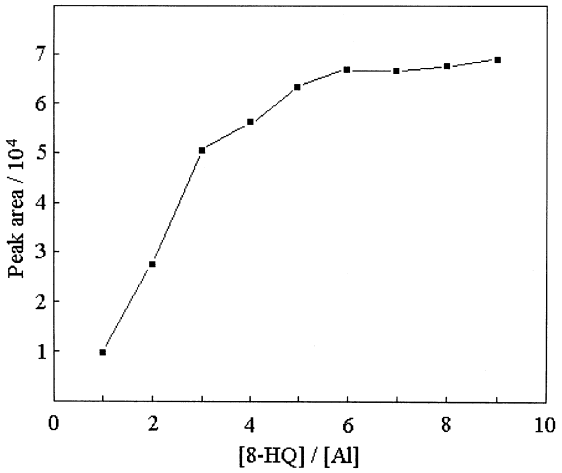

Figure 1. Dependence of peak area on molar ratio of 8-HQ to Al in pre-column reaction medium. Column PC8-10, 10 µm, 25 cm × 4.6 mm I.D. Column temperature 30°C. Mobile phase 40% methanol 40% ethyl acetate 20% water containing 25 mmol/L lithium lactate (pH 8.0). Flow rate 1.0 mL/min. Injection volume 10 µL. Wavelength used for UV detection 390 nm.

toluene as a reference substance. The result, given in Table 1, for 5–25 μg of Al in 5 mL of standard solution was between 97.61–103.07%, which was better than that (92.7–106.8%) obtained using chloroform as an extracting agent.[16]

Effect of Water Content in Mobile Phase

The effect of water content in mobile phase, on the chromatographic behavior of Al-8-HQ, was investigated in the range of 10–25% (v/v) in a mixture of methanol and ethyl acetate (1 : 1 v/v). The retention time of the chelate and toluene increased in different degrees with increasing water content, as shown in Fig. 2. In order for good separation and in view of decomposition of the complex in the hydrophobic column by water,[6,13,14] 20% water was chosen.

Effects of pH and Ionic Strength of Mobile Phase

It is observed from Fig. 3 that changing the pH (6.5–8.5) of mobile phase with Tris-HCl had significant influence on the capacity factor of both Al-8-HQ and toluene. In order to perform the separation and maintain the stability of the complex, the pH of mobile phase was adjusted to 8.0, that of the sample solution prior to extraction. The effect of lithium lactate concentration (10–50 mmol/L) on the peak shape of Al-8-HQ was also investigated in considerable detail, as indicated in Fig. 4. Although, no significant change in retention time was found, this reagent was a necessary addition to the mobile phase in order to prevent decomposition of the complex. In the absence of it, peak

Table 1. Extraction efficiency of Al-8-HQ.

Al amount (μg)	Extraction efficiency (%)	Average (%)	RSD (%)
5	97.61		
10	99.61		
15	99.89	100.08	1.95
20	100.20		
25	103.07		

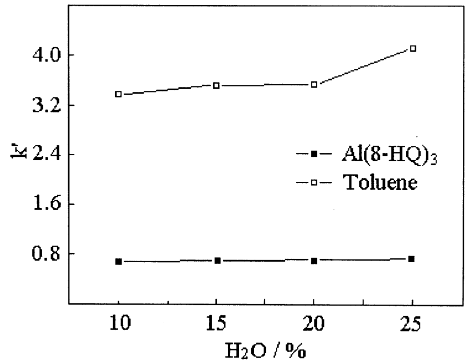

Figure 2. Dependence of k' value on water content in mobile phase. Other conditions as in Fig. 1.

height of Al-8-HQ was small and the peak shape changed randomly. The optimum concentration selected was, therefore, 25 mmol/L.

Detection Wavelength

It is well known that 380–400 nm is the most suitable detection wavelength for HPLC determination of Al-8-HQ.[11–14,16] We found, experimentally, that at 390 nm, Al-8-HQ has absorption maximum and 8-HQ has less contribution to the chelate absorption in weak basic medium. The detection was carried out at this wavelength.

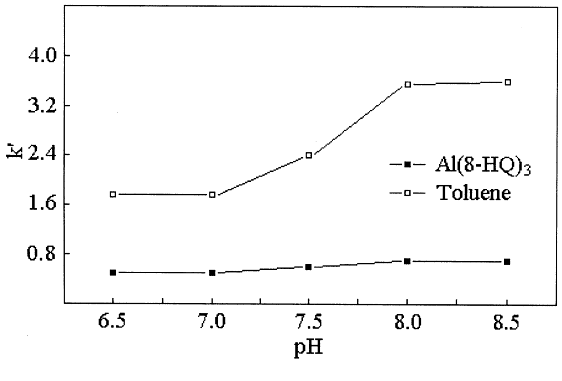

Figure 3. Dependence of k' value on pH of mobile phase. Other conditions as in Fig. 1.

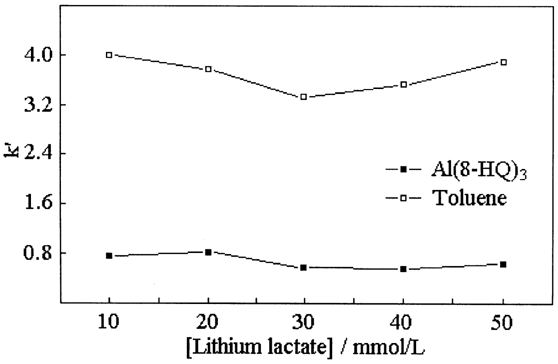

Figure 4. Dependence of k' value on lithium lactate concentration in mobile phase. Other conditions as in Fig. 1.

Chromatogram, Linear Range, and Detection Limit

The typical chromatogram obtained from an extraction solution of Al-8-HQ with toluene was shown in Fig. 5b. Under the optimum condition the chelate, the ligand, and toluene were well separated. The linear relationship of peak area vs concentration of Al standard is obtained from 0.04 μg/mL to 1.0 μg/mL with a 10 μL injection, that is $A = -76.42 + 25515.93C$ with

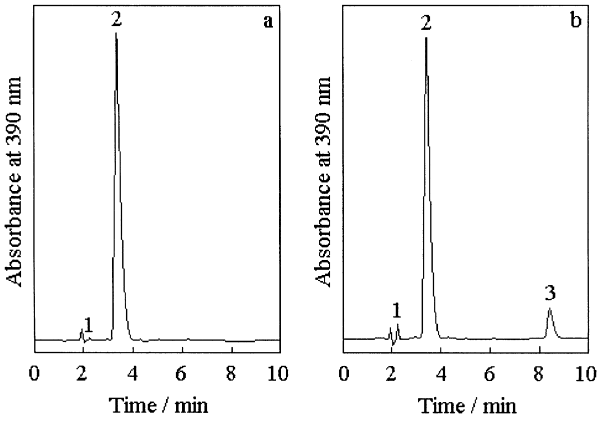

Figure 5. Typical chromatograms for Al-8-HQ chelate. Other conditions as in Fig. 1. (a) pure Al-8-HQ in methanol; (b) sample after extraction with toluene. Peaks: (1) 8-HQ; (2) Al-8-HQ; (3) toluene.

Table 2. Determination of Al in real samples ($n = 3$).

		Determined			Found		
Sample number	Sample	Concentration (μg/mL)	RSD[a] (%)	Added (μg/mL)	Concentration (μg/mL)	RSD (%)	Recovery (%)
1	Wahaha purified drinking water	0.022					
2	Tianyudi mineral drinking water	0.022					
3	Nanjing tap water	0.029					
4	Nantong tap water	0.046					
5	Nanjing tap water boiled 5 min with Al vessel	0.117		0.100	0.216	1.58	99.1
				0.200	0.312	1.38	95.7
6	Nanjing tap water boiled 30 min with Al vessel	0.133	2.14				
7	Nanjing tap water boiled 120 min with Al vessel	0.260	0.47	0.200	0.441	1.37	92.7
				0.300	0.558	0.64	99.2
8	Nanjing pond water	0.310					
9	Yangzhou lake water	0.403		0.200	0.592	0.48	97.3
				0.400	0.807	0.08	101.0
10	Suinin river water	0.501		0.250	0.740	0.42	97.8
				0.500	1.002	1.00	100.2

[a] No RSD data represent the average of two determinations.

correlation coefficient of 0.99997. The detection limit, defined as the concentration where the peak height was three times the background, was 0.008 μg/mL Al (0.08 ng in injection volume).

Effects of Foreign Ions

A number of foreign ions were examined for interference. For the determination of 0.08 μg/mL (ca. 0.003 mmol/l) Al, the results showed that a 500-fold excess of Ca^{2+} or Mg^{2+}, 250-fold excess of citrate, and 200-fold excess of F^- did not interfere. A 20-fold tartrate, 12-fold of Zn^{2+}, 10-fold of Cu^{2+} or Ni^{2+}, and equal molar of Fe^{3+} or Co^{2+} interfered. Because the amounts of the major interfering ions present in drinking and natural waters are very low, in fact, they will not cause any interference for determining Al.

Analysis of Real Samples

The analytical results of various drinking and natural waters were listed in Table 2. They are in good agreement with those obtained by ICP-AES. In order to evaluate the validity of analytical data, known amounts of Al were added to partial samples and then the analysis performed in the usual way. The recovery lay between 92.7–101.0% and confirms that there is no problem duo to the matrix effects. The RSDs were less than 2.1% for most of the sample analysis and recovery tests, but those from extraction with chloroform were 2.0–7.1%.[16] These indicated that the proposed method is more reliable for determining Al in various water samples.

CONCLUSION

This paper is the first report demonstrating that toluene is used as the extracting agent of Al-8-HQ prior to HPLC analysis. The extraction with toluene not only increased the sensitivity of Al compared to that obtained without extraction procedure, but also improved the extraction efficiency and the precision of determination compared to the data achieved by extraction with chloroform. The reliability of the developed method was confirmed by determination of Al performed on various real drinking and natural water samples.

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REFERENCES

1. Jeffries, D.S.; Hendershot, W.H. Aluminum geochemistry at the catchment scale in watersheds influenced by acidic precipitation. In *The Environmental Chemistry of Aluminum*, 2nd Ed.; Sposito G., Ed.; CRC Press: Boca Raton, FL, 1996; 279–301.
2. Exley, C. *Aluminum and Alzheimer's Disease*; Elsevier Science B.V.: Amsterdam, 2001; 1 pp.
3. Anderson, J.R.; Reimert, S. Determination of aluminum in human tissues and body fluids by zeeman-corrected atomic absorption spectophotometry. Analyst **1986**, *111* (6), 657–660.
4. Pierson, K.B.; Evenson, M.A. Measurement of aluminum in neuronal tissues using electrothermal atomization absorption spectrophotometry. Anal. Chem. **1986**, *58* (8), 1744–1748.
5. Hirata, S.; Umezaki, Y.; Ikeda, M. Determination of chromium (III), titanium, vanadium, iron (III), and aluminum by inductively coupled plasma atomic emission spectrometry with an on-line preconcentrating ion-exchange column. Anal. Chem. **1986**, *58* (13), 2602–2606.
6. Baiocchi, C.; Saini, G.; Bertolo, P.; Cartoni, G.P.; Pettiti, G. Pre-column chelation with 8-hydroxyquinoline for the simultaneous determination of metal ions by reversed-phase high-performance liquid chromatography. Analyst **1988**, *113* (5), 805–807.
7. Kaneko, E.; Hoshino, H.; Yotsuyanagi, T.; Gunji, N.; Sato, M.; Kikuta, T.; Yuasa, M. Determination of aluminum in the human serum of a dialysis patient by ion-pair reversed-phase partition high-performance liquid chromatography. Anal. Chem. **1991**, *63* (20), 2219–2222.
8. Akama, Y.; Tong, A. High-performance liquid chromatographic determination of aluminum and iron (III) in solar salt in the form of their 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone chelates. J. Chromatogr. **1993**, *633* (1–2), 129–133.
9. Inoue, K.; Zenki, M. Reversed-phase high-performance liquid chromatography of aluminum with 2-hydroxy-5-sulfoaniline-n-salicylidene as a fluorometric reagent. Bunseki Kagaku **1993**, *42* (12), 805–809.
10. Zhou, C.Y.; Wu, J.; Chi, H.; Wong, M.K.; Koh, L.L.; Wee, Y.C. High performance liquid chromatographic determination of aluminum in natural waters in the form of its lumogallion chelate. Talanta **1995**, *42* (3), 415–422.

11. Lopez, A.; Rotunno, T.; Palmisano, F.; Passino, R.; Tiravanti, G.; Zambonin, P.G. Simultaneous determination of chromium (III), aluminum (III) and iron (II) in tannery sludge acid extracts by reversed phase high-performance liquid chromatography. Environ. Sci. Technol. **1991**, *25* (7), 1262–1266.
12. Ryan, E.; Meaney, M. Determination of trace levels of copper (II), aluminum (III) and iron (III) by reversed-phase high-performance liquid chromatography using a novel on-line sample preconcentration technique. Analyst **1992**, *117* (9), 1435–1439.
13. Nagaosa, Y.; Kawabe, H.; Bond, A.M. Separation and simultaneous determination of aluminum, iron and manganese in natural water samples by using high-performance liquid chromatography with spectrophotometric and electrochemical detection. Anal. Chem. **1991**, *63* (1), 28–33.
14. Lian, H.Z.; Bi, S.P.; Chen, Y.J.; Dai, L.M.; Cao, M.; Li, H.M.; Tian, L.C. Direct determination of aluminum in drinking and natural waters as 8-hydroxyquinoline chelate by RP-HPLC. J. Liq. Chrom. Rel. Technol. **2001**, *24* (2), 215–228.
15. Haddad, P.R.; Valeenuwat, S. Reversed-phase high performance liquid chromatography of 8-hydroxyquinoline complexes of Mo (VI), Al (III), Co (III), and Cu (II). HRC CC **1986**, *9* (2), 127–128.
16. Tang, Y.; Huang, J.; Zou, G.W.; Shi, J.; Bi, S.P. Extraction and HPLC analysis of tri(8-quinolinolato)aluminum. Chinese J. Inorg. Chem. **2000**, *16* (4), 637–640.
17. Miller, C.C.; Chalmers, R.A. Micro-analysis of silicate rocks: Part IV. The determination of alumina. Analyst **1953**, *78* (933), 686–694.
18. Mendelowitz, A. The use of oxine in the analysis of commercial aluminum sulphate–a statistical approach. Anal. Chim. Acta **1956**, *14* (3), 235–242.

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