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Speciation of Aluminum in Drink Samples by 8-Hydroxyquinoline Loaded Silylanization Silica Gel Microcolumn Separation with Off-Line ICP-MS Detection

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A technique using a flow injection microcolumn separation coupled with ICP-MS detection has been developed for the speciation of Al in drink samples. The retention behaviors of different Al species were studied with 8-hydroxyquinoline (8-HQ) loaded silylanization silica gel as the packing material and inorganic acid (HNO_3) as the elution. The results indicated that in a pH range of 5.0 to 8.0, all labile monomeric Al species were retained on the microcolumn while nonlabile monomeric Al species were directly passed through the column. Various Al species after separation were detected by ICP-MS. The detection limit of 0.2 ng mL^{-1} and a relative standard deviation (RSD) of 4.2% at 10 ng mL^{-1} ($n = 11$) were achieved, and the recoveries for the spiked samples were 95−108%. The proposed method has been applied to the analysis of Al species in tea infusions, coffee, and tap waters with satisfactory results. The results obtained by this method were compared with that obtained by the cation exchange microcolumn separation and ICP-MS detection system, and some valuable conclusions were drawn.

KEYWORDS: Al; speciation; microcolumn; ICP-MS; 8-hydroxyquinoline

INTRODUCTION

Much interest has been raised by the toxicity and biological effects of Al in recent years (*1*−*5*). Some studies suggest that Al species may be accumulated in the brain via different routes (drinking waters, food, and medicines) and cause serious neurotic diseases (*6*, *7*). Furthermore, this metal ion has been considered as a possible cause of Alzheimer's disease (*8*, *9*). Further studies have revealed that the toxicity and biological effects of aluminum are strongly dependent on its speciation (*10*, *11*), and the labile monomeric Al species (including Al^{3+}, $AlOH^{2+}$, $Al(OH)_2^{+}$, and very labile Al complexes like AlF^{2+} and AlF_2^{+}) have been found to be primarily toxic for aquatic systems.

The labile Al and nonlabile Al species can be classified according to the following separation steps: (1) The retained Al species are considered as the labile Al when the solution is passed through a cation-exchange resin (*12*−*14*). It is possible to obtain separation of labile inorganic monomeric Al species (including cationic Al species, Al−hydroxide complexes, and Al−fluoride and Al−sulfate) from more stable organic complexes Al. (2) The labile Al species include the Al species reacted with the chelating reagents, and retained on the column when the solution is through a chelating resin column (*15*, *16*).

The chelating reagent 8-hydroxyquinoline (8-HQ) has high affinity for Al, and it has been widely applied to Al trace analysis (*12*, *17*−*22*). Milacic et al. (*12*) used butyl acetate to extract the $Al(oxinate)_3$ complex, and the labile Al was then determined by spectrophotometric detection. Fairman et al. (*20*) used an Amberlite XAD-2 resin in a minicolumn to adsorb the $Al(oxinate)_3$ formed at pH 5.0, and the retained "fast reactive" Al was then eluted with 1.0 mol L^{-1} HCl and determined by ICP-MS. Simpson et al. (*17*) reported a labile Al speciation analysis procedure in which a selective reaction was performed in a 22 μL column reactor.

The aim of this paper is to develop a method for Al speciation by using a 8-hydroxyquinoline (8-HQ) loaded silylanization silica gel microcolumn separation/ICP-MS detection system. The retention behaviors of different Al species on the microcolumn and its affecting factors were investigated. A comparative study on different packed materials (cation-exchange resin and 8-HQ silylanization silica gel) for speciation of Al was also performed. The proposed method was applied to the analysis of Al species in drink samples, and some conclusions were drawn.

MATERIAL AND METHODS

Instrumentation. A HP 7500a ICP-MS (Agilent) system was used for the determination of Al. The optimum operation conditions are summarized in **Table 1**. The pH values were measured with a Mettler Toledo 320-S pH meter (Mettler Toledo Instrument (Shanghai) Co. Ltd.) supplied with a combined electrode. A HL-2 peristaltic pump (Shanghai Qingpu Huxi Instrument Factory, Shanghai, China) with 0.5 mm i.d. PTFE tubing and a self-made PTFE microcolumn (20 mm × 3.0 mm i.d.) were used in the separation process. A model 800 centrifuge (Shanghai Instruments Factory, Shanghai, China) was used for centrifugation of sample infusions. The instrument and the operation conditions of ICP-AES were described in previous papers (*23*, *24*).

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Table 1. Optimum Operating Conditions for Determination of Al

Plasma		Ion Lenses	
incident power	1200 W	extract 1	−143.5 V
rf matching	1.6 V	extract 2	−67 V
carrier gas (Ar) flow rate	1.16 L min^{-1}	Einzel 1, 3	−94 V
		Einzel 2	0 V
coolant gas (Ar) flow rate	15 L min^{-1}	plate bias	0 V
		omega bias	−27 V
sampling depth	7 mm	omega (+)	2.7 V
sample uptake rate	0.4 mL min^{-1}	omega (−)	−0.1 V
		QP focus	7.3 V
Q-Pole		Detector	
AMU gain	126	discriminator	8.7 mV
AMU offset	126	analog	1460 V
axis gain	0.9998	pulse HV	900 V
axis offset	0.02		
QP bias	1.2 V	integration time	0.1 s
		nebulizer	Babington
ion mass	27 *m/z*	torch	Fassel (quartz)
data acquisition	single ion monitoring		
sampler	Ni, 1.0 mm diam orifice		
skimmer	Ni, 0.4 mm diam orifice		

Standard Solution and Reagents. Suprapure acids and water doubly distilled in quartz were used for the preparation of samples and standard solutions. All other chemicals were of analytical-reagent grade or better.

Aluminum Standards. A stock Al solution (1 g L^{-1} Al) of Al was prepared in a 100 mL calibrated flask by dissolving 1.3904 g of $Al(NO_3)_3 \cdot 9H_2O$ in doubly distilled water. A stock Al fluoride solution (10 μg mL^{-1} Al) was made weekly by mixing 0.1554 g of NaF and 1.0 mL of stock Al solution in a 100 mL flask (100:1 fluoride to Al molar ratio). A stock Al citrate solution (10 μg mL^{-1} Al) was made weekly by mixing 1.0882 g of $Na_3Cit \cdot 2H_2O$ and 1.0 mL of stock Al solution in a 100 mL flask (100:1 citrate to Al molar ratio). A stock Al catechol solution (10 μg mL^{-1} Al) was made weekly by mixing 0.4486 g of catechol and 1.0 mL of stock Al solution in a 100 mL flask (100:1 catechol to Al molar ratio). A stock 8-HQ solution (5.0×10^{-2} mol L^{-1}) was prepared by dissolving of 0.2258 g of 8-HQ in ethanol and diluting to 100 mL with ethanol. The working standard solutions were prepared by dilution with water each day.

Buffer Solutions. Potassium biphthalate (0.05 mol L^{-1}) buffer solution was prepared by dissolving 1.0211 g of potassium biphthalate in 100 mL of doubly distilled water and adding either 0.5 mol L^{-1} HNO_3 or 0.5 mol L^{-1} KOH to adjust the pH in the range 5.0−6.5. TRIS-HNO_3 (0.05 mol L^{-1}) buffer solution was prepared by dissolving 0.6057 g of tris(hydroxymethyl)aminomethane (TRIS) in 100 mL of doubly distilled water and adding either 0.5 mol L^{-1} HNO_3 or 0.5 mol L^{-1} KOH to adjust the pH in the range 7.0−8.0.

Silylanization silica gel (100−150 mesh) (Shanghai Reagent Factory, Shanghai, China) was immersed in ethanol and 1 mol L^{-1} HNO_3 for 24 h, respectively, then filtered and washed with doubly distilled water until neutral, and dried prior to storage for use. The commercial No. 724 weakly acidic cation-exchange resin (200−300 mesh) (Hangzhou Zhengguang Resin Co., Hangzhou, China) was immersed in 3 mol L^{-1} HCl and 0.5 mol L^{-1} NaOH for 24 h, respectively, then filtered and washed with doubly distilled water until neutral, and dried prior to storage for use.

Microcolumn Preparation and Cleaning Procedures. *8-HQ Silylanization Silica Gel Microcolumn.* A total of 60 mg of silica gel was filled into a PTFE microcolumn (20 mm × 4.0 mm i.d.) plugged with a small portion of glass wool at both ends to prevent the escape of the packing material from the microcolumn. It was found experimentally that the packed microcolumn contained trace amounts of Al; when the column was used for separation of Al species after directly coated with 8-HQ, the recoveries obtained for labile Al were found to be much higher than 100%. In order to solve this problem, an efficient cleaning of the silica gel microcolumn before separation was necessary. For this purpose, 10 mL of 5×10^{-4} mol L^{-1} 8-HQ solution was passed through the microcolumn at a flow rate of 1.0 mL min^{-1}, followed by 10 mL of 1.0 mol L^{-1} HNO_3, and then the microcolumn was washed with doubly distilled water until neutral. The cleaning was repeated three times until the trace Al could not be detected. Finally, the microcolumn was coated by passing 10 mL of 5×10^{-4} mol L^{-1} 8-HQ solution through the microcolumn at the flow rate of 1.0 mL min^{-1}, and then preequilibrated with buffer solution of the desired pH.

Cation Exchange Microcolumn. The cation exchange microcolumn used in this paper and its operating procedure were described previously (*24*).

To avoid contamination by external Al, all the containers before use were treated with 10% HNO_3 for 24 h, rinsed well with water, and dried at room temperature.

Sample Preparation. *Tea (or Coffee) Infusions.* Portions (1.000 g) of tea leaves (or coffee) (dried at 80 °C for 4 h,140 mesh) were transferred into a beaker. Twenty-five milliliters of boiling distilled water was poured into the beaker, and the solution was stirred in a boiling water bath for 15 min. After a 15 min wait for cooling, the infusion was centrifuged (4000 rpm, 20 min) and filtered through a 0.45 μm membrane filter (Tianjin Jinteng Instrument Factory, Tianjin, China). The sample was diluted to 50 mL with deionized water. The pH of the infusions was measured as 5.5−6.0. Blank experiments were carried out using the same procedure without tea leaves (or coffee). Analyses were done within 1 day.

Sample Decomposition. Portions (50 mg) of samples were mixed with 1.0 mL of concentrated HNO_3 in a PTFE beaker and deposited overnight. After the mixture was heated until nearly dry, 0.5 mL of $HClO_4$ was added, the mixture was heated to near dryness for the destruction of residual organic substances, and the residual solution was dissolved and diluted to 50 mL with distilled water for ICP-MS analysis of the total Al.

Tap Waters. Before analysis, the tap water was filtered through a 0.45 μm membrane filter, and 100 mL of tap water was collected to be used. The pH of the tap water was measured as 7.0−8.0.

Spiked Samples. Appropriate amounts of Al solution (0.1 mL) were added to 10 mL of tea infusion or tap water, and the spiked sample was mixed well before separation. The pH of the spiking Al solutions was adjusted to 5.5.

Recommended Procedure. The soluble Al was detected by ICP-MS directly, and 5 mL of solution was passed through the 8-HQ silylanization silica gel microcolumn by using a peristaltic pump at a flow rate of 1.0 mL min^{-1}. The species (nonlabile Al) that passed directly through the column were collected, and the retained species (labile Al) were eluted with 1.0 mol L^{-1} HNO_3 solution. Separated Al species were determined by ICP-MS.

For comparison, the cation exchange microcolumn and ICP-AES determination were used for speciation of Al in drinks and similar separation processes were performed. Another 5 mL solution was passed through the cation exchange microcolumn by using a peristaltic pump at a flow rate of 1.0 mL min^{-1}, the nonlabile Al species that passed directly through the column were collected, and the retained labile Al species were eluted with 1.0 mol L^{-1} HCl solution. Separated Al species were determined by ICP-AES.

RESULTS AND DISCUSSION

Effect of pH on the Retention of Different Al Species. In order to study the effect of pH on the retention of various Al species, the Al^{3+}, Al fluoride, Al citrate, and Al catechol were selected as the representatives of free ion, inorganic complex, and organic complex, respectively. The experiment was performed with 100 ng/mL (as Al) of different Al species standard solutions by adjusting pH from 5 to 8, and the results are shown in **Figure 1**. It is obvious that in the pH range of 5.0−8.0, free ion Al^{3+} and Al fluoride were retained on the 8-HQ silica gel column with a quantitative recovery (93−99%). However, organic complexes (Al citrate and Al catechol) were not retained by the 8-HQ silica gel column, and they passed directly through the column. It is already known that the Al species may exist as the forms of Al^{3+}, $AlOH^{2+}$, $Al(OH)_2^+$, and $Al(OH)_4^-$ in Al stock solutions when pH varies from 5.0 to 8.0, and when the

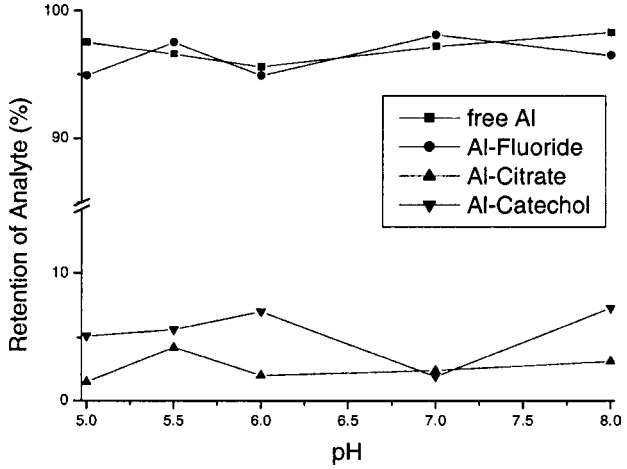

Figure 1. The effect of pH on the retention of Al species on the 8-HQ silica gel column.

Table 2. Elution of Al with Different HNO_3 Concentration

HNO_3 concn (mol L^{-1})	0.05	0.1	0.5	1.0
recovery of Al (%)	62.5	77.5	92.1	102.6

ligands were added to this solution and exceeded greatly (the ratio of ligands/Al was 100 in this paper), the Al complexes were the main species in the solutions. In our previous study (*24*), it was found that $AlF_{3...6}$ may be the dominating species when fluoride was excessive in the Al fluoride system and neutral $Al(Cit)^0$ or negatively charged $Al(Cit)^{x-}$ was prevailing when citrate was excessive in the Al citrate system. Hence, the difference in retention behavior for various Al species on an 8-HQ silica gel microcolumn can be easily explained. As an excessively aggressive ligand, 8-HQ could react with free Al and inorganic Al while it could not sequester Al from more stable organic Al complexes in a short time.

Thus, it could be concluded that the labile Al inorganic species (free ion Al^{3+} and Al fluoride) and the nonlabile organic Al species (Al citrate and Al catechol) could be separated effectively by the proposed method.

Effect of Eluant Concentration. In this study, HNO_3 was used as eluant reagent to elute the retained Al on the microcolumn at a flow rate of 1.0 mL min^{-1}, and the effect of eluant concentration (HNO_3) on the recovery of various Al species was studied. The results listed in **Table 2** indicate that the retained Al could be eluted quantitatively with the concentration of HNO_3 higher than 0.5 mol L^{-1}. In this study, 1.0 mol L^{-1} HNO_3 was selected to guarantee a complete elution.

Comparison of the Two Procedures. Both the 8-HQ silica gel microcolumn system and the cation exchange microcolumn system were employed for the speciation of aluminum in tap water and tea, and the analytical results are given in **Table 3**. As could be seen, the analytical results for different Al species in tea infusions obtained by both separation systems were accordant, while there was an obvious difference in nonlabile monomeric Al for tap water. The nonlabile monomeric Al in tap water obtained by the 8-HQ silica gel microcolumn system was higher than that obtained by the cation exchange microcolumn system, while no obvious difference for labile monomeric Al in tap water by both separation systems was observed. The reason for this is unclear at present; some further research work should be done.

Detection Limit and Precision. The limit of detection is defined as the analyte concentration that gives a signal that is three times the standard deviation of the background. The limit of detection (3σ) of ICP-MS for Al was 0.2 ng mL^{-1}, and the relative standard deviation was 4.2% (c = 10 ng mL^{-1}, n = 11). The limit of detection (3σ) of ICP-AES for Al was 100 ng mL^{-1}, and the relative standard deviation was 3.7% (c = 5 μg mL^{-1}, n = 11).

Table 3. Comparison of the 8-HQ Silica Gel Microcolumn Separation System (X) and the Cation Exchange Microcolumn Separation System (Y) for Speciation of Al in Tap Water and Tea Infusion (μg mL^{-1})

			nonlabile monomeric Al		labile monomeric Al	
sample	added	soluble Al	X	Y	X	Y
tap water A		0.119	0.012	0.0035	0.114	0.120
	0.1	0.224	0.016	0.0048	0.215	0.219
	0.5	0.633	0.044	0.014	0.605	0.632
	1.0	1.11	0.050	0.020	1.062	1.03
tap water B		0.384	0.035	0.0062	0.358	0.380
	0.1	0.490	0.051	0.026	0.430	0.469
	0.5	0.894	0.052	0.018	0.798	0.852
	1.0	1.43	0.107	0.018	1.32	1.44
Wufen green tea[a]		0.469	0.485	0.474		
	0.5	0.986	0.937	0.911	0.110	0.134
	1.0	1.48	1.36	1.18	0.144	0.221
	10.0	10.30	9.89	9.53	0.687	0.867
Deyu black tea[b]		8.61	8.58	8.42	0.416	0.518
	0.5	9.07	9.01	9.04	0.730	0.631
	1.0	9.53	9.03	8.98	0.855	0.906
	10.0	18.51	17.16	17.62	1.42	1.17

[a] Produced in Hubei Province. [b] Produced in Jiangxi Province.

Table 4. Results of the Speciation Analysis of Aluminum in Real Drink Samples (μg g^{-1}, n = 3)

sample	pH	total Al	soluble Al	nonlabile monomeric Al	labile monomeric Al
Jiao Guo Lan tea[a]	6.3	299	5.05	4.17	0.960
Luo HanGuo tea[b]	5.2	553	123	117	14.2
Que Chao coffee[c]	5.9	73.3	6.60	6.30	0.420
Wufen green tea[a]	5.5	92.8	23.4	24.5	–
Deyu black tea[d]	5.9	1640	430	429	20.8

[a] Produced in Hubei Province. [b] Produced in Hongkong. [c] Produced in Jiangxi Province. [d] Produced in Fujiang Province.

Table 5. Results for the Speciation Analysis of Al in Tea Infusion and Tap Water and the Recovery for the Total Soluble Al (μg mL^{-1}, n = 3)

sample	added	soluble Al	nonlabile monomeric Al	labile monomeric Al	recovery (%)
tap water A		0.119	0.0120	0.114	
	0.1	0.224	0.0160	0.215	105.0
	0.5	0.633	0.0440	0.605	102.8
	1.0	1.11	0.0500	1.06	99.1
tap water B		0.384	0.035	0.358	
	0.1	0.490	0.051	0.430	106.0
	0.5	0.894	0.052	0.798	102.0
	1.0	1.43	0.107	1.32	104.6
Wufen green tea		0.469	0.485		
	0.5	0.986	0.937	0.110	103.4
	1.0	1.48	1.36	0.144	101.1
	10.0	10.3	9.89	0.687	98.3
Deyu black tea		8.61	8.58	0.416	
	0.5	9.07	9.01	0.730	92.0
	1.0	9.53	9.03	0.855	92.0
	10.0	18.5	17.2	1.42	99.0

Sample Analysis. The proposed procedure of the 8-HQ silica gel microcolumn separation system combined with ICP-MS detection was applied to separate and determine soluble Al,

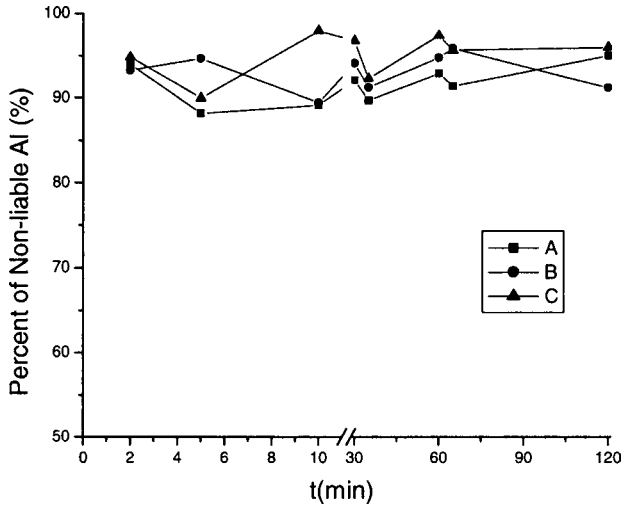

Figure 2. The effect of the deposited time on the distributions of Al species in green tea infusion after the free Al was added into the green tea infusion. **A**: Added 0.5 μg mL^{-1} Al^{3+}. **B**: Added 1.0 μg mL^{-1} Al^{3+}. **C**: Added 10.0 μg mL^{-1} Al^{3+}.

Table 6. The Comparative Data of the Different Detections (μg mL^{-1}, $n = 3$)

		soluble Al		nonlabile monomeric Al		labile monomeric Al	
sample	added	ICP-MS	ICP-AES	ICP-MS	ICP-AES	ICP-MS	ICP-AES
Wufen green tea		0.469	0.55	0.485	0.52		
	0.5	0.986	1.03	0.937	1.03	0.110	0.14
	1.0	1.48	1.40	1.36	1.30	0.144	0.14
	10.0	10.30	10.42	9.89	10.03	0.687	0.70
Deyu black tea		8.61	8.68	8.58	8.60	0.416	0.37
	0.5	9.07	9.00	9.01	9.00	0.730	0.51
	1.0	9.53	9.47	9.03	9.04	0.855	0.75
	10.0	18.51	18.55	17.16	17.05	1.42	1.38

labile monomeric Al, and nonlabile monomeric Al in tea and coffee infusions, and the analytical results are listed in **Table 4**.

The recoveries for the spiked tap waters and tea infusions were studied, and the results are shown in **Table 5**. As could be seen, recoveries in the range of 92−106% were obtained for both tap water and tea infusions.

To evaluate the reliability of this method, the Al species (soluble Al, nonlabile monomeric Al, and labile monomeric Al) in tea infusions were analyzed by both ICP-MS and ICP-AES, and their results are shown in **Table 6**. As could be seen, a good agreement of the analytical results obtained by both methods was obtained.

From the results given in **Table 4** and **Table 5**, the following conclusions can be drawn:

(1) The distribution of the Al species and the total Al in different kinds of drinks or the same kinds of drinks produced in different places were different; the total Al concentration in black tea was higher than that in other drinks.

(2) The nonlabile monomeric Al species (i.e., organic Al complexes) were the major species in the studied drinks. In other words, the labile monomeric Al (as a toxic component) only made up less than 10% of soluble Al for tea and coffee. On the contrary, over 90% of soluble Al in tap waters was labile monomeric Al.

(3) Most of the added free Al could be converted into nonlabile Al after it was added into the tea infusions (**Table 5**). In contrast, when the free Al was added to the tap water, most of the free Al still existed as the form of labile Al. In order to clarify the reason for this phenomenon, the effect of deposited time on the distribution of Al species after the free Al was added into the green tea infusion was studied. **Figure 2** shows the dependence of Al species distributions on the time for green tea infusion. It was found that most of the added free Al could be converted into nonlabile Al in a very short time. The possible reason is that there are great amounts of organic compounds in tea infusions, and these organic compounds could react quickly with the added free Al to form the organic Al complexes.

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