Microemulsion extraction separation and determination of aluminium species by spectrofluorimetry

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ABSTRACT

A simple and sensitive microemulsion extraction separation method was developed for the speciation of aluminium in tea samples by spectrofluorimetry. With 8-hydroxyquinoline (8-HQ) as the chelating agent and Triton X-100 Winsor II microemulsion as the extractant, separation of aluminium species in different pH solutions was achieved by microemulsion extraction. The formation of microemulsion, the conditions of extraction and determination of aluminium species were studied. The results showed that, the contents of aluminium species in tea leaves and infusions samples, such as total aluminium, total soluble aluminium, total granular aluminium, inorganic aluminium except Al-F, and (Al-F + Al-org), were obtained successfully under the optimal conditions. The limit of detection was $0.23\,\mu g\,L^{-1}$ in pH 9.5 solution, and $0.59\,\mu g\,L^{-1}$ in pH 6.0 solution respectively; the precision (RSD) for 11 replicate measurements of $10\,\mu g\,L^{-1}$ aluminium was 2.1% in pH 9.5 solution, and 2.8% in pH 6.0 solution respectively; the recoveries for the spiked samples were 96.8–103.5%. The proposed method is simple and efficient, which has been applied to the speciation of aluminium in tea samples with satisfactory results.

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1. Introduction

Aluminium has always been considered as non-toxic elements in the past. However, under certain conditions, aluminium (Al) tends to form some species that are potentially toxic to living organisms [1]. Recent studies have shown that abnormal high aluminium levels are linked to some diseases such as dementia dialitica, osteomalacia, and Alzheimer's disease [2,3]. The toxicity of aluminium depends on its species in the environmental and biological systems. Determination of total aluminium has little importance, since the toxicity of different species of aluminium varies considerably. Biological toxicology has proved that the toxicity of inorganic aluminium (Al^{3+}, $AlOH^{2+}$, $Al(OH)_2^{+}$, and so on) is the greatest, aluminium fluoride (Al-F) and organic aluminium (Al-org) toxicity are substantially reduced or even disappear [4]. Therefore, speciation of aluminium in the environmental and biological systems is a very important subject of concern at present.

The most frequently used procedure for the speciation of aluminium is 8-hydroxyquinoline (8-HQ)/cation-exchange method by Driscoll [5]. However, the method still has some disadvantages: the hazardous organic solvent methylisobutylketone (MIBK) is used; time-consuming; and great error for the indirect determination of inorganic monomeric aluminium. Therefore many scientists have been exploring other effective and simple methods for spe-

ciation of aluminium. Ion-exchange chromatographic methods, which are based on the selective sorption of some aluminium species on the resins, have been developed for the speciation of aluminium in nature waters, soil solutions and other aqueous systems [6–10]. Size exclusion chromatography (SEC) enables separation of aluminium species on the basis of their molecular masses [11], however the SEC method is not selective enough. Fast protein liquid chromatography (FPLC) with inductively coupled plasma atomic emission spectrometry (ICP-AES) [12] or inductively coupled plasma mass spectrometry (ICP-MS) detection [13] was reported to enable speciation of some positively charged monomeric aluminium in soil extracts and human serum, however the coupling instrumentation was very complicated and cost too much. Flow injection analysis methods [14] seem to be of special importance for the determination of aluminium species; they allow highly reproducible and comparatively short experimental times, which can be coupled to a range of detection systems. Capillary zone electrophoresis [15,16] possesses a distinct advantage for separation of fluoro and oxalato aluminium complexes, however, which cannot achieve the separation of other inorganic and organic aluminium complexes. Compared to these methods abovementioned, microemulsion extraction method for the separation of aluminium species is simple and efficient, which has been applied in metal ions extraction as separation media [17–20].

Microemulsion usually consists of water, organic solvent (oil) and surfactant, occasionally including alcohol as cosurfactant. It is defined as a system formed by dispersion of microdroplets of two immiscible liquids, stabilized by an interfacial membrane formed

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by surfactant and cosurfactant, which is thermodynamically stable, homogeneous and optically isotropic [21]. Generally speaking, only if the microemulsion is oil continuous, it can be used to separate material from aqueous phase. Thus, the extraction of metal ions by using Winsor II system, which is w/o microemulsion coexisting with a water phase, is often very effective to accelerate extraction and improve extract ability. The increase of the extraction rate is explained by an enormous rise of the micro-interfacial surface area in the w/o microemulsion phase and the participation of microemulsion globes that transport metal ions from the aqueous phase to the organic phase [22,23].

Tea is one of typical Al-accumulating plants. Tea infusion is a widely consumed beverage, so tea drinking is the major source of dietary Al intake [24]. In general, the total concentration of Al in tea infusions is in the range $1–6\,mg\,L^{-1}$, probably more than 90% of this Al is organic form [25]. The distribution of Al species in tea infusion is changeable with time. Investigations have indicated that the main species of aluminium existed in tea infusion included polyphenolic complexes, Al fluoride, Al oxalate, free Al^{3+} and its hydrolysate, etc. In a recent paper [26], some investigations of speciation of aluminium in tea leaves and tea infusion were reviewed, demonstrating that at the moment it was very difficult to give a consistent picture of the speciation of aluminium in this drink.

Aluminium (III) can be bound to 8-hydroxyquinoline (8-HQ), and form a steady complex with fluorescence under certain experimental conditions. In the present work, adjusting the acidity of the sample solution to appropriate pH value separately, different Al species in tea infusion sample could react with 8-HQ to form Al-8-HQ complexes, which were separately extracted in the Winsor II microemulsion phase, and determined by the spectrofluorimetry. Potential factors affecting the extraction of Al species by microemulsion were investigated in detail.

2. Experimental

2.1. Apparatus

A model F-4500 FL fluorophotometer (Hitachi Ltd., Japan) with a 1-cm quartz cell was employed to measure the fluorescence. A model pHS-3C digital pH meter (Shanghai Precision & Scientific Instrument Co., Ltd., Shanghai, China) was used for all pH measurements. A DK-S26 super electrical thermostat (Shanghai Experimental Instruments Co., Ltd., Shanghai, China) was used to assist the phase separation. The instrument and the operation conditions of ICP-AES were according to the literature [27].

2.2. Reagents and solutions

All of the chemicals used were at least of analytical grade and were purchased from Shanghai Chemicals Co., Ltd. (Shanghai, China) unless otherwise stated. Doubly distilled water (DDW) was used throughout the entire study. A stock Al solution ($1.0\,g\,L^{-1}$ Al) was prepared from high purity Al powder by adding HCl solution ($6.0\,mol\,L^{-1}$) and DDW. A stock Al fluoride solution ($10\,\mu g\,mL^{-1}$ Al) was prepared from NaF and Al stock solution (100:1 fluoride to Al molar ratio). A stock Al citrate solution ($10\,\mu g\,mL^{-1}$ Al) was prepared from $Na_3Cit\cdot2H_2O$ and Al stock solution (100:1 citrate to Al molar ratio). A stock Al catechol solution ($10\,\mu g\,mL^{-1}$ Al) was prepared from catechol and Al stock solution (100:1 catechol to Al molar ratio). Working standard solutions were prepared by appropriate stepwise dilution of stock solution. A $0.02\,mol\,L^{-1}$ 8-HQ solution was prepared by dissolving appropriate amounts of 8-HQ in $2\,mol\,L^{-1}$ acetic acid solution. Ammonium acetate buffer solutions ($1.0\,mol\,L^{-1}$) were prepared by dissolving appropriate amounts of NH4Ac in DDW, and adjusting to pH 2.0–6.5 with HAc

or to pH 7.0–12.0 with $NH_3\cdot H_2O$. Triton X-100 w/o microemulsion was made of Triton X-100 (Sigma), n-pentanol, n-hexane and DDW (3.0:15.0:1.5:4.0, mass).

2.3. Microemulsion extraction procedure

For the microemulsion extraction, a certain amount of tea infusion sample, 1.5 mL 8-HQ solution, 2.0 mL Triton X-100 microemulsion and 1.5 mL buffer solution (HAc-NH4Ac of pH 6.0 for inorganic aluminium except Al-F (Al_i), or $NH_4Ac-NH_3\cdot H_2O$ of pH 9.5 for total soluble aluminium (Al_a)) were added into a 25-mL color tube. The mixture solution was diluted to the mark with DDW, shaken, and stood in a thermostated water bath at 60 °C for 15 min, then cooled to room temperature. The supernatant microemulsion phase was transferred directly to a 1-cm quartz cell for a fluorescence measurement at emission wavelength 514.0 nm, keeping the excitation wavelength 372.8 nm.

2.4. Determination of total aluminium in tea leaves

1 g of dried tea leaves (dried at 105 °C for 2 h) was placed in a corundum crucible, heated at 650 °C and maintained 1 h. The ash of sample was mixed with 4 mL of concentrated HNO_3 solution. The sample solution was steamed to about 2 mL, and then added 1 mL concentrated $HClO_4$ solution to make the solution give off white fume. After cooling, the residue was dissolved with 1 mL HCl solution ($6\,mol\,L^{-1}$), then transferred quantitatively into a 250-mL volumetric flask and diluted to the volume with DDW. After this treatment, 2.0 mL of the solution was used to determine the concentration of total aluminium determination in tea leaves.

2.5. Speciation of aluminium in tea infusions

1 g of dried tea leaves was placed in a beaker. 20 mL of hot DDW was poured into the beaker and the solution was heated up to boiling point. After cooling, the extract was filtered through a 0.45-μm Millipore filter. 2.0 mL of tea infusion was used to determine the Al_i and Al_a according to Section 2.3.

For determination of total aluminium (Al_t) in tea infusion, the tea infusion sample was acidified to pH 1.0 by adding concentrated HNO_3 solution and left stand for more than 24 h, then extracted at pH 9.5 and measured according to Section 2.3.

The concentration of granular aluminium (Al_g) was obtained as the difference between Al_t and Al_a, The concentration of (Al-F + Al-org) was obtained as the difference between Al_a and Al_i.

3. Results and discussion

3.1. Fluorescence spectra and selecting of the extraction system

In the experiment, some extraction systems, such as Triton X-100 w/o microemulsion, cetyltrimethylammonium bromide (CTAB) w/o microemulsion, sodium dodecyl sulphate (SDS) w/o microemulsion, chloroform [28], and Triton X-100 cloud point extraction (CPE) system [29], were studied. The fluorescence spectra of Al-8-HQ complex in the different media were shown in Fig. 1. The excitation wavelength (λ_{ex}), the emission wavelength (λ_{em}) and fluorescence intensity (F) were listed in Table 1.

From Fig. 1 and Table 1, Triton X-100 w/o microemulsion had the highest sensitivity, followed by the chloroform system, Triton X-100 CPE system, CTAB w/o microemulsion; the sensitivity of SDS w/o microemulsion was the lowest. The sensitivity of Al-8-HQ complex in various w/o microemulsion was different, which was mainly related to surfactants and complex. In the Triton X-100 w/o microemulsion, the nitrogen atom of 8-HQ could combine with the hydroxyl of Triton X-100 through hydrogen bonds. So Al-8-HQ
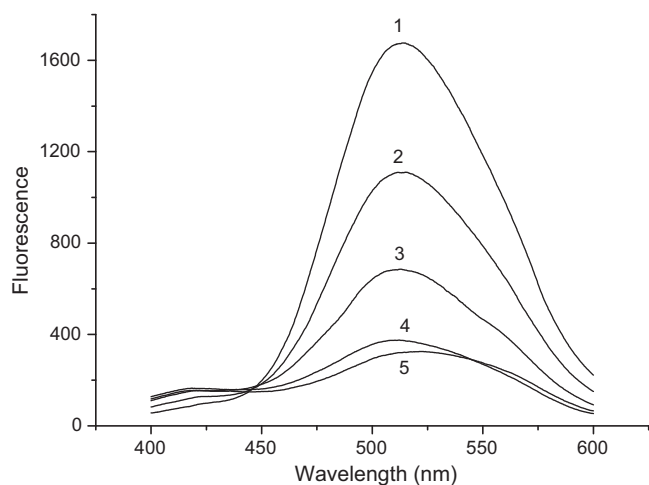
Fig. 1. Fluorescence spectrum of Al–8-HQ in different media (1) Triton X-100 w/o microemulsion; (2) chloroform; (3) Triton X-100 CPE system; (4) CTAB w/o microemulsion; (5) SDS w/o microemulsion. Other conditions: 1.2×10^{-3} mol L^{-1} 8-HQ, pH 9.5, equilibration temperature 60 °C.

Fig. 2. Effect of pH on the extraction of Al-8-HQ. Other conditions: 1.2×10^{-3} mol L^{-1} 8-HQ, 2.0 mL Triton X-100 w/o microemulsion, equilibration temperature 60 °C. Fluorescence conditions: λ_{ex} 372.8 nm, λ_{em} 514.0 nm.

complex could be adsorbed to the micro-droplet interface and solubilized into the mono-layer, the amounts of solubilization was increased. However, the microdroplet interface of CTAB or SDS w/o microemulsion was charged with positive or negative charge, while the Al-8-HQ complex was without charge. It is disadvantage for the solubilization of Al-8-HQ complex in CTAB or SDS w/o microemulsion. In addition, because Al-8-HQ complex was weakly polar, the complex could be dissolved in the weakly polar system to some extent, such as chloroform or Triton X-100 CPE system.

3.2. Factors affecting of the microemulsion extraction

3.2.1. Effect of pH

In the microemulsion extraction process of Al-8-HQ, the acidity of the solution played a unique role on the complex formation and subsequent speciation of Al. Fig. 2 shows the effect of pH value of solution on the extraction of Al-8-HQ. The results showed that, when the acidity was at pH 6.0 and 9.5, fluorescence of Al-8-HQ in the microemulsion phase reached the maximum.
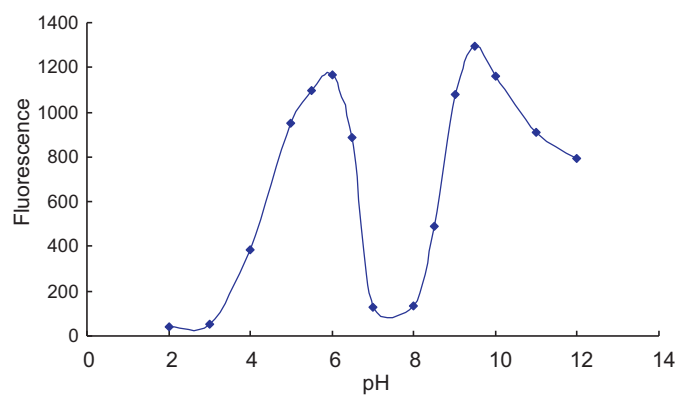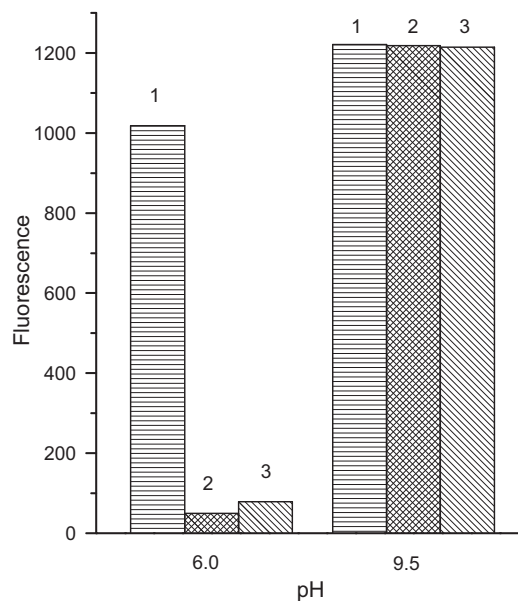
In order to study the effect of pH on the complexation ability of 8-HQ with aluminium species, the free Al^{3+}, Al fluoride, Al citrate, Al catechol were selected as the representatives of Al species in tea infusions. The results (as shown in Fig. 3) showed that, when the acidity was at pH 6.0, 8-HQ could react with all hydrated aluminium, hydroxy aluminium complexes, and other inorganic aluminium, such as Al chloride, Al sulphate and so on, but almost not reacted with aluminium fluoride and organic aluminium, such as Al polyphenol, Al citrate and so on. However, when the acidity was at pH 9.5, 8-HQ could react with all total soluble aluminium, including inorganic aluminium, aluminium fluoride and organic aluminium. So it would provide a good procedure to the speciation of aluminium at

different pH values of the sample solution without any pretreatment.

3.2.2. Effect of the concentration of fluorine and organic compounds

Tea is a kind of plants that can concentrate fluorine. Fluorine level in tea leaves changes in the range 3.2–260 mg kg^{-1} and 97% of the fluorine releases into the tea infusions [25]. Fluorine and aluminium can form six kinds of stable complexes, AlF^{2+}, AlF$_2^+$, AlF$_3$, AlF$_4^-$, AlF$_5^{2-}$ and AlF$_6^{3-}$, whose stability constants are between 10^6 and 10^{19} [30]. In the study, the effect of the concentration of F$^-$ on the extraction of Al-fluoride was investigated. When the concentration of fluorine was in the range of 0.5–400 mg L^{-1}, 8-HQ could not react with aluminium fluoride to form Al-8-HQ complex at pH 6.0, but aluminium fluoride could be almost entirely converted into Al-8-HQ complex at pH 9.5.

In addition, as the representative of organic compounds in tea, the effects of the concentration of tannic acid, tartaric acid or citric acid were studied. The results showed that, when the concentration of each organic compound was over 10 mg L^{-1}, aluminium and

Table 1
Fluorescence intensity in different media.

Medium	λ_{ex} (nm)	λ_{em} (nm)	F[a]	F[b]
Triton X-100 w/o microemulsion	372.8	514.0	1676	132
Chloroform	374.0	515.0	1110	94.5
Triton X-100 CPE	371.4	512.8	685.5	74.6
CTAB w/o microemulsion	370.0	512.2	375.7	27.8
SDS w/o microemulsion	374.2	523.0	325.7	36.0

[a] Fluorescence intensity of Al-8-HQ in different media.
[b] Fluorescence intensity of 8-HQ in different media.

Fig. 3. Comparison of the extraction of aluminium species in pH 6.0 or 9.5 solution (1) inorganic aluminium except Al-F, (2) Al-org, (3) Al-F. Other conditions: 1.2×10^{-3} mol L^{-1} 8-HQ, 2.0 mL Triton X-100 w/o microemulsion, equilibration temperature 60 °C. Fluorescence conditions: λ_{ex} 372.8 nm, λ_{em} 514.0 nm.
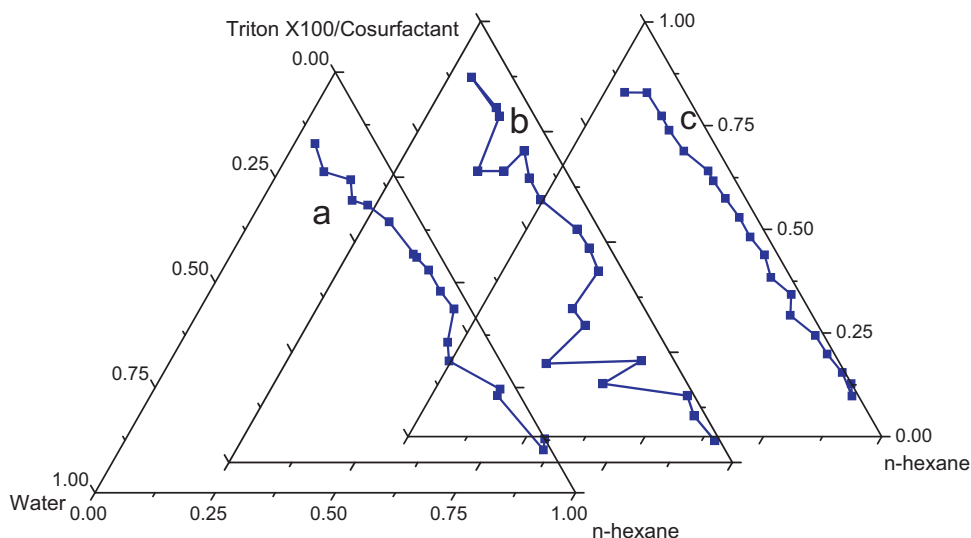
Fig. 4. Effect of the alcohols on the microemulsion region (a) n-butanol/Triton X-100 = 4.0; (b) n-octanol/Triton X-100 = 4.0; (c) n-pentanol/Triton X-100 = 4.0.

organic compound could form stable complex, which would be only extracted effectively at pH 9.5. However, tea contains a large number of organic compounds, particularly polyphenols [31]. Such a large number of organic compounds all can form stable complexes with aluminium.
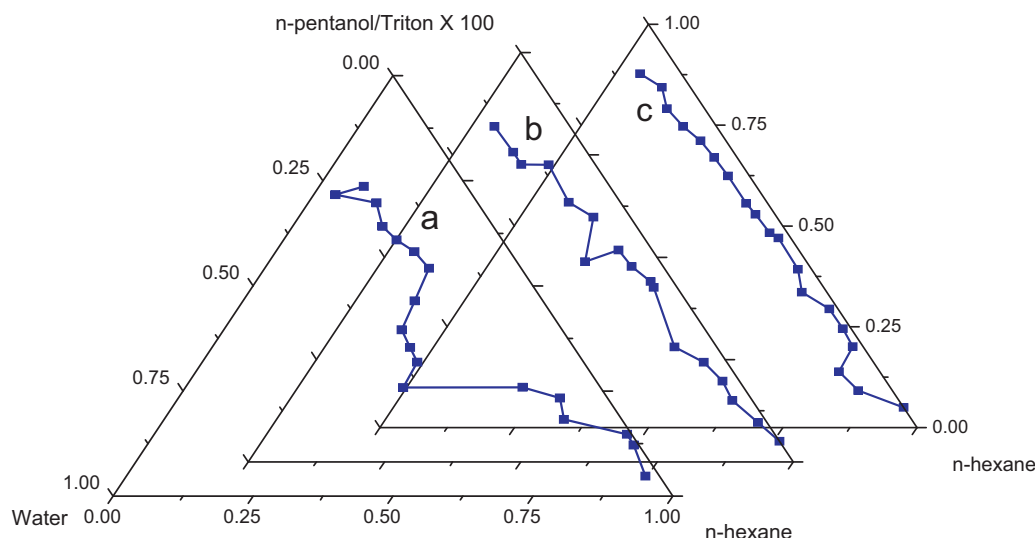
3.2.3. Effect of the microemulsion formation

Some parameters known to have important influence on the existence domain of microemulsion, such as types of cosurfactants and cosurfactant/surfactant molar ratio (C/S), were investigated.

The cosurfactant is usually a non-ionic molecule that associates to the surfactant, whose purpose is to neutralize the repulsive effect among the surfactant polar heads, allow the formation of a membrane between the micelle and the continuous phase of the microemulsion. In the study, n-butanol, n-pentanol and n-octanol were tested. The results (as shown in Fig. 4) showed that the microemulsion area was the largest when the cosurfactant was n-pentanol. This result could be explained by the Bos law [32] that, when the length of alcohol chain and length of oil chain equal to the non-polar chain of surfactant, the microemulsion mixed membrane would be arranged more neatly and firmly.

For stabilizing the micelles in the microemulsion region, the cosurfactant often requires excessive amount, the C/S ratios of 1.0, 3.0 and 6.0 were investigated. It was observed that the microemulsion existence domain increased with the increase in the C/S ratio (Fig. 5). However, according to the further experiment results, the extraction efficiency of Al-8-HQ was the largest when the C/S ratio was 4.0. So the C/S ratio of 4.0 was used in the subsequent experiments.

3.2.4. Effect of amounts of the reagents

Fig. 6a showed the effect of the concentration of chelating agent 8-HQ on the microemulsion extraction efficiency for Al species. The extraction efficiency for Al species increased as the concentration of 8-HQ from 2.0×10^{-4} mol L^{-1} to 1.2×10^{-3} mol L^{-1} at pH 9.5, and then kept almost constant with further increase in the 8-HQ concentration up to 2.0×10^{-3} mol L^{-1}. While at pH 6.0, the extraction efficiency for Al species kept almost constant when the concentration of 8-HQ was more than 1.2×10^{-3} mol L^{-1}. Amounts of buffer solution were added variously to adjust the sample solution appropriate pH value, the results were shown in Fig. 6b, the maximum and stable fluorescence intensity was gained in the range

Fig. 5. Effect of the C/S ratios on the microemulsion region (a) n-pentanol/Triton X-100 = 1.0. (b) n-Pentanol/Triton X-100 = 3.0. (c) n-Pentanol/Triton X-100 = 6.0.
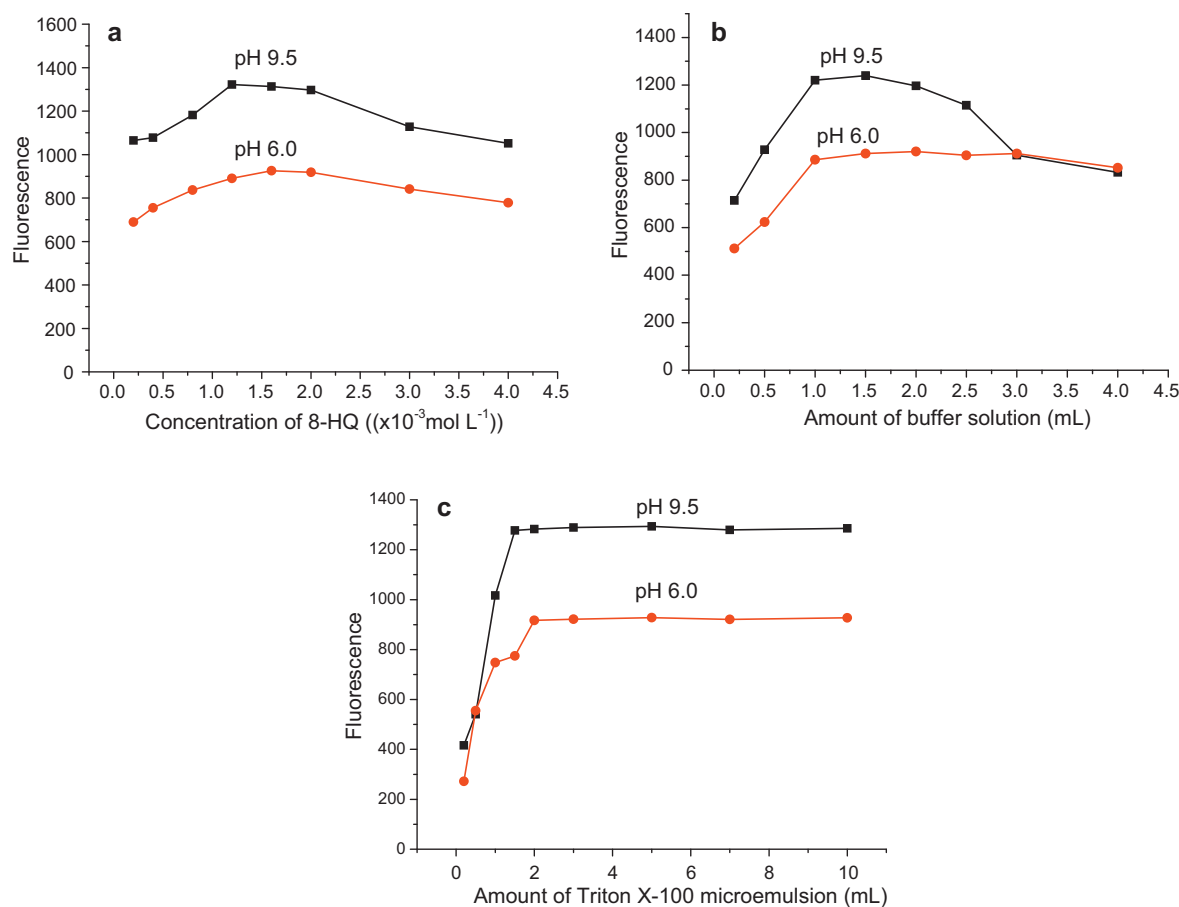
Fig. 6. Effect of the 8-HQ concentration (a), amounts of buffer solution (b), and Triton X-100 microemulsion (c) on the extraction of Al species. Other conditions: equilibration temperature 60 °C. Fluorescence conditions: λ_{ex} 372.8 nm, λ_{em} 514.0 nm.

of 1.0–3.0 mL of HAc–NH$_4$Ac buffer solution of pH 6.0, and in the range of 1.0–2.0 mL of NH$_3$·H$_2$O–NH$_4$Ac buffer solution of pH 9.5. When the volume of the Triton X-100 microemulsion was in the range of 2.0–10.0 mL, the extraction efficiency for Al species was nearly 100% at pH 6.0 or 9.5 (as shown in Fig. 6c). Therefore, an 8-HQ concentration of 1.2×10^{-3} mol L^{-1}, 1.5 mL of HAc-NH$_4$Ac or NH$_3$·H$_2$O–NH$_4$Ac, and 2.0 mL of Triton X-100 microemulsion were employed for all speciation of Al in subsequent experiments.

3.2.5. Effect of temperature of phase separation

It would take more than 60 min to microemulsion phase separation fully at room temperature. The higher the temperature was, the phase separation of microemulsion was faster, but the extraction efficiency would remain basically unchanged. When the tempera-

Table 2
Influence of foreign ions.

Foreign ion	Tolerance limits (mg L^{-1})	Foreign ion	Tolerance limits (mg L^{-1})
Fe^{3+}	40	Pb^{2+}	32
Cu^{2+}	80	Ni^{2+}	20
Mg^{2+}	20	F$^-$	400
Zn^{2+}	32	Citrate	200
Cd^{2+}	80	Tartrate	320
Ag$^+$	48	Tannic acid	400
Mn^{2+}	40	Catechin	400
Ca^{2+}	16	Gallic acid	320

Table 3
Comparison of the present method with some recent studies on determination of aluminium reported in the literature.

Method	System	Medium pH	LOD (μg L^{-1})	RSD (%)	PF	Detection	Reference
Coprecipitation	Co^{2+}/8-HQ	8.0	0.2	<6	50	UV–vis	[33]
Solid phase extraction	Amberlite XAD-1180/PV	8.0–9.0	0.021	<10	150	GFAAS	[34]
Kinetic-spectrophotometry	Nile Blue A/KBrO$_3$	0.2 mol L^{-1} H$_2$SO$_4$	34	1.7	–	UV–vis	[35]
On-line liquid–liquid extraction	8-HQ/methylisobutylketone	8.0	0.3	3	3	GFAAS	[36]
Cloud point extraction	8-HQ/Triton X-114	6.2	0.79	2.7	10	Spectrofluorimetry	[37]
Cloud point extraction	Morin/1-undecanol	4.5	0.8	4.5	128	ICP-OES	[38]
Cloud point extraction	PAN/Triton X-114	8.0	0.06	3.6	34.8	GFAAS	[39]
Cloud point extraction	CAS/CTAB, Triton X-114	6.0	0.52	2.85	20	Spectrophotometry	[40]
Flow injection micro column separation	8-HQ/silylanization silica gel	5.0–8.0	0.2	4.2	–	ICP-MS	[41]
Microemulsion extraction	8-HQ/TritonX-100 w/o microemulsion	6.0, 9.5	pH 6.0:0.59	pH6.0:2.8	50	Spectrofluorimetry	This work
			pH 9.5:0.23	pH 9.5:2.1			

Table 4
Results of the speciation of aluminium in tea leaves and tea infusions.

Sample	Total Al in tea leaves ($\mu g\,g^{-1}$)	Al species in tea infusions ($\mu g\,L^{-1}$)						Recovery (%)
		Added	Total Al	Total soluble Al	Inorganic Al except Al-F	Al fluoride and organic Al	Granular Al	
Zhuyeqin tea	462	–	124.0	57.2	9.0	48.2	66.8	
		50	174.8.	108.1	9.3	97.8	66.7	101.6
Puer tea	1240	–	406.5	194.4	42.6	151.9	212.1	
		100	505.9	293.6	42.9	250.7	212.3	99.2
Maojian tea	506	–	152.5	72.3	11.6	60.7	80.2	
		50	203.1	123.7	12.1	111.6	79.4	102.8
Tieguanyin tea	1125	–	372.5	249.4	52.0	197.4	123.1	
		100	475.6	352.9	53.1	299.8	122.7	103.5
Bai tea	620	–	217.8	96.3	19.2	77.1	121.5	
		100	315.4	193.1	20.0	173.1	122.3	96.8

Table 5
Results of the speciation of aluminium in the tea leaf certified reference material and its tea infusion.

Sample	Total Al in tea leaves ($\mu g\,g^{-1}$)			Al species in tea infusions ($\mu g\,L^{-1}$)								
	X[a]	Y[a]	Certified	Total Al		Total soluble Al		Inorganic Al except Al-F		Al fluoride and organic Al		Granular Al	
				X	Y	X	Y	X	Y	X	Y	X	Y
GBW10016	930 ± 20	935 ± 30	940 ± 90	300.5	304.2	213.6	209.8	42.8	41.4	170.8	168.4	86.9	94.8
GBW07605	2860 ± 50	2900 ± 50	3000	953.0	950.6	458.7	461.2	83.9	82.0	374.8	379.2	494.3	489.4

X, the proposed method; Y, ICP-AES.

[a] Average of six runs ± standard deviation.

Table 6
Comparison of the present method with some recent studies on speciation of aluminium reported in the literature.

Technique	Aluminium species	Remarks	Reference
Driscoll's fraction scheme	Labile mononuclear Al, non-mononuclear Al species and the acid-soluble fraction in aqueous solutions	Combination of 8-HQ, column cation-exchange, acid digestion techniques and GFAAS determination for speciation of Al	[5]
Ion-exchange chromatography	Free aluminium (Al^{3+}), fluoride complexes (AlF^{2+} and AlF_2^+) and other forms of aluminium in nature waters	Cation-exchange HPLC and the fluoride ion-selective electrode, and fluorometric detection of the aluminium–lumogallion complex	[7]
Chelating ion-exchange chromatography	Sorption and separation of simple and toxic species of aluminium in nature waters	Iontosorb oxin and iontosorb salicyl resins FAAS determination for speciation of Al	[9]
Ion exchange separation	Total Al, polyphenolic Al, and cationic Al in tea infusions	Amberlite XAD-7 resin for separation of polyphenolic Al, Chelex-100 resin for separation of cationic Al	[10]
Size exclusion chromatography and cation exchange fast protein liquid chromatography	Al-fluoro, Al-oxalato, and Al-citrate species in forest soil extracts	Size exclusion chromatography with UV and ICP-AES detection and cation exchange fast protein liquid chromatography with ETAAS detection	[12]
Flow injection microcolumn separation	Soluble Al, labile monomeric Al, and nonlabile monomeric Al in drink samples	8-Hydroxyquinoline loaded silylanization silica gel microcolumn separation with offline ICP-MS detection	[41]
Adsorption stripping voltammetry	Labile monomeric Al, total monomeric Al, acid reactive Al, nonlabile monomeric Al, acid soluble Al in natural water	Speciation scheme based on the competitive complexation with Al-solochrome violet RS	[42]
Cation-exchange HPLC	Inorganic monomeric Al, organic monomeric Al, and colloidal mineral Al in stream waters	Fluorescence detection of the Al–lumogallion complex	[43]
Speciation of Al in soil samples by different reagent extraction procedures	Water-soluble Al, exchangeable Al, weakly organically bound Al, and total organically bound Al	Water-soluble Al extracted by water, exchangeable Al extracted by KCl, weakly organically bound Al extracted by $CuCl_2$, total organically bound Al extracted by $Na_4P_2O_7$	[44]
Microemulsion extraction	Total soluble Al, granular Al, inorganic Al except Al-F, Al fluoride + organic Al	Fluorescence detection of the Al-8-HQ complex in microemulsion	This work

ture was over 50 °C, and the incubation time was more than 10 min, phase separation would be fully. So, in the experiment, the water bath temperature of 60 °C and the incubation time of 15 min were used for the phase separation process.

3.3. Evaluation of interferences

The interferences of potential coexisting ions on the determination of 0.4 μg mL^{-1} aluminium (III) were investigated. The tolerance limits, defined as interferential concentration changing the analyte signal by 10%, were presented in Table 2. The results indicated that the contents of these coexisting ions in tea infusion samples would not exceed the tolerance limits. Therefore, the present method could be employed directly.

3.4. Analytical figures of merit

Under the optimum conditions, the fluorescence intensities (F) of Al-8-HQ complexes at pH 6.0 or 9.5 were measured, and the calibration graphs of F against concentration of aluminium (III) were constructed. The results showed that, when at pH 9.5, F was directly proportional to the concentration of aluminium (III) in the range of 0.80–640 μg L^{-1}, the linear regression equation was $F = 4.618\rho$ (μg L^{-1}) + 392.8 ($r = 0.9964$), the limit of detection (LOD) was 0.23 μg L^{-1}, which was calculated as the 3σ of the reagent blank, the relative standard deviation (RSD) was 2.1% ($n = 11$). While at pH 6.0, F was directly proportional to the concentration of aluminium (III) in the range of 2.0–320 μg L^{-1}, the linear regression equation was $F = 6.267\rho$ (μg L^{-1}) + 230.7 ($r = 0.9953$), the limit of detection (LOD) was 0.59 μg L^{-1}, the relative standard deviation (RSD) was 2.8% ($n = 11$). The preconcentration factor, calculated as the concentration ratio of analyte in the final microemulsion extract and in the initial solution, was 50 for aluminium.

Table 3 compares the characteristic data of the present method with those of recent reported methods on determination of alu-

minium. Some parameters obtained are comparable to those presented by other methods. The present work has relatively low LOD and RSD when compared to other methods [35–38,40,41]. Preconcentration factor (PF 50) is relatively high enough when compared to some of the others methods [35–37,39–41]. In addition, most of the cited methods are more complicated than this method, namely application of this method is simpler and takes less time.

3.5. Application to speciation of aluminium in real samples

The proposed method was applied for the speciation of aluminium in the tea leaves and infusions samples according to the recommended procedures. The analytical results and spike recoveries were shown in Table 4. As could be seen, the recoveries of spiked samples ranged from 96.8% to 103.5%. To further prove the validity of the proposed method, certified reference materials (CRMs were provided by the National Research Center, China) of GBW10016 and GBW07605 tea leaves sample were analyzed and the determination results of Al content in tea leaves were in good agreement with the certified values, moreover, the analytical results of Al content in CRMs and Al species in CRMs infusions determined by the present method were in good agreement with those determined by ICP-AES (Table 5). In addition, it could be found from Tables 4 and 5 that, the aluminium content in tea leaves is relatively high, about 30% of aluminium from dry tea leaves were transferred into tea infusions according to the experimental operation; from the species analysis, a considerable part of aluminium in tea infusions is present as complexes with organic compounds or aluminium fluoride, which is less toxicity.

4. Conclusions

In this work, we proposed a novel idea for the separation of Al species by Triton X-100 Winsor II microemulsion system

and determination by spectrofluorimetric method, which was based on the different competitive complexation behavior of 8-hydroxyquinoline (8-HQ) that ligands to Al at different pH values. Inorganic aluminium except Al-F (Al_i) and total soluble aluminium (Al_a) in the tea infusions could be extracted respectively in the Winsor II microemulsion phase by the form of Al-8-HQ at pH 6.0 and 9.5. The total aluminium (Al_t) in tea infusions was extracted at pH 9.5 and measured after the tea infusion sample was acidified to pH 1.0 and left stand for more than 24 h. The concentration of granular aluminium (Al_g) was obtained as the difference between Al_t and Al_a. The concentration of (Al-F + Al-org) was obtained as the difference between Al_a and Al_i. Compare to other recent studies on speciation of aluminium reported in the literature (Table 6), species of aluminium in tea samples, which included total soluble Al, granular Al, inorganic Al except Al-F, Al fluoride + organic Al, were separated and determined comprehensively by the present method. Moreover, in the paper, the most important species – inorganic aluminium (Al^{3+}, $AlOH^{2+}$, $Al(OH)_2^+$, and so on), which was thought to the greatest toxic species of aluminium [4], was directly separated and determined. In addition, the present method is easier to perform and less time-consuming, which has been applied to the speciation of aluminium in tea samples successfully.

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