



Preconcentration, separation and spectrophotometric determination of aluminium(III) in water samples and dialysis concentrates at trace levels with 8-hydroxyquinoline–cobalt(II) coprecipitation system

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ABSTRACT

A separation–preconcentration procedure was developed for the determination of trace amounts of aluminium in water samples and dialysis concentrates by UV–vis Spectrophotometry after coprecipitation using 8-hydroxyquinoline (8-HQ) as a chelating agent and Co(II) as a carrier element. This procedure is based on filtration of the solution containing precipitate on a cellulose nitrate membrane filter following aluminium(III) coprecipitation with Co/8-HQ and then the precipitates together with membrane filter were dissolved in concentrated nitric acid. The metal contents of the final solution were determined by UV–vis Spectrophotometry with Erio Chrome Cyanine-R standard method. Several parameters including pH of sample solution, amount of carrier element and reagent, standing time, sample volume for precipitation and the effects of diverse ions were examined. The enrichment factor was calculated as 50 and the detection limits, corresponding to three times the standard deviation of the blank ($N: 10$), was found to be $0.2 \mu\text{g L}^{-1}$. The accuracy of the method was tested with standard reference material (CRM-TMDW-500) and spiked addition. Determination of aluminium(III) was carried out in sea water, river water, tap water and haemodialysis fluids samples. The recoveries were $>95\%$. The relative standard deviations of determination were less than 6%.

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1. Introduction

Aluminium is a non-essential, toxic metal to which humans are frequently exposed by the use of aluminium-containing drugs, inhalation of atmospheric dust, food, drinks, etc. This element has been involved as a causative factor in several clinical and neuropathological diseases, particularly in patients with chronic renal failure. Elevated levels of aluminium have been implicated in the etiology of Alzheimer's disease, Parkinson's disease, Parkinson–Guam's disease, amyotrophic lateral sclerosis, diabetes and cancer [1,2].

Because of aluminium accumulation of in the tissues of some patients with chronic renal failure, also monitoring of aluminium concentration in dialysis fluids has increasing attentions in the last two decades. The European Committee established that diluted dialysis fluids should not contain aluminium concentrations higher than $10 \mu\text{g L}^{-1}$ [3–7].

The toxicity of aluminium is much acute in aquatic species. Most biologically active and environmentally significant aluminium forms are the monomeric positively charged hydroxyl ions ($\text{Al}(\text{OH})_2(\text{H}_2\text{O})_4^+$). These species have been found to be primarily responsible for aluminium toxicity [8–10].

Normally aluminium is found at low levels in most drinking waters because aluminium is still used as a flocculating agent in potable water treatment units. The maximum permissible content of aluminium in drinking water is 0.2 mg L^{-1} [11]. Therefore, there is a strong need for aluminium monitoring in water samples [12,13] and also other samples.

At the moment, the widely used analytical techniques for the detection of the aluminium are the graphite furnace atomic absorption spectrometry (GFAAS) and inductively coupled plasma-atomic emission spectrometry (ICP-AES) [14–17]. Despite advances having been made in detection instrumentation, trace metal analysis most often requires some form of separation and preconcentration methods to remove interfering matrices and ensure the level of analyte is detectable [18]. Thus, determinations of aluminium in different samples using separation and preconcentration steps are still necessary and coupling of them with simple and less expensive determination techniques such as UV–vis spectrophotometry

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is very attractive [13,19]. Some of the major methods of separation and preconcentration involve evaporation, volatilization, coprecipitation, cloud point extraction, solvent extraction or solid-phase extraction [18,20–28].

Coprecipitation has also an important place in the preconcentration and separation methods due to its some advantages including simplicity, high preconcentration factors, low consumption of organic solvent and short analysis time period for the procedures [29–33]. In the coprecipitation procedure, a precipitate was occurred by the combination of a carrier element and a suitable inorganic or organic ligand. Various carrier elements including copper, nickel, aluminium, erbium, magnesium, indium, samarium, etc. have been used for the coprecipitative preconcentration and separation of heavy metal ions at traces levels [34–39]. Inorganic ligands like hydroxide, thiocyanate and organic ligands like various dithiocarbamates, 5-methyl-4-(2-thiazolylazo) resorcinol, rubeanic acid, etc. have been used for this purpose [40–44].

For the present work, 8-hydroxyquinoline (8-HQ) and Co(II) were selected as organic reagent and carrier element, respectively. According to our literature survey, this combination is not used for the coprecipitation of aluminium ion, until now. This method has a main advantage: a simple UV–vis spectrophotometer can be easily operated without needing expensive and complex instruments for the determination of aqueous samples having complicate matrix and low concentration of aluminium(III).

The experimental conditions for coprecipitation of the aluminium(III) onto Co/8-HQ, including pH, sample volume, amount of carrier element, matrix ions and standing time have been optimised. This method has several advantages in comparison with the other coprecipitation methods. It has lower detection limit (DL) and relative standard deviation (RSD) values. The method is simple, reliable, fairly rapid, economic and precise. The recoveries of aluminium(III) in the presence of the most common matrix elements containing the alkaline and alkaline earth metals and transition metals were fairly good.

2. Experimental

2.1. Apparatus

Absorbance measurements were made using a Dr. Lange Cadas 200 UV–vis Spectrophotometer with 1.0-cm quartz cells. The instrumental parameters were those recommended by the manufacturer. A pH meter, Hanna pH-211 digital glass electrode, was employed for measuring pH values in the aqueous solution. Distilled/deionized water was obtained from Sartorius Milli-Q system (arium® 611UV). MSE Mistral 2000 model centrifuge was employed for centrifugation of solutions.

2.2. Reagents and solutions

All chemicals used in this work were of analytical reagent grade and were used without further purification. Distilled/deionized water was used for all dilutions. All glassware and plastic used were soaked in 1:10 HNO₃–H₂O solution for 1 day before used then cleaned repeatedly with distilled/deionized water. For storage of water samples, polypropylene bottles (5 L) were used prior to analysis. 8-HQ, HNO₃ and NaOH was supplied by Merck. Stock solutions of studied metal (aluminium(III) as a Al(NO₃)₃ salt) and carrier element (Co(II)) were produced by diluting a stock solution of 1000 mg L⁻¹ of the given elements supplied by Sigma and Aldrich. Diluted HNO₃ and NaOH solution were used for pH adjustments.

Trace metal in drinking water standard (CRM-TMDW-500) was obtained from High-Purity Standard, Inc.

2.3. Preconcentration work

25.0 mL portion of an aqueous solution containing 1 µg of aluminium(III) was placed in a centrifuge tube. The pH of solution was adjusted to 8.0. Then 1.0 mL of 1000 mg L⁻¹ of cobalt (II) as a carrier element and 1 mL of 8-HQ solution prepared in ethyl alcohol (0.5% w/v) were poured into the tube and sample solution was diluted to 50 mL with distilled water. After 10 min, the solution was centrifuged at 2750 rpm for 20 min. The supernatant was removed. The precipitate in the tube was dissolved with 1 mL of concentrated HNO₃ and evaporated to dryness onto the hot plate. The residue was dissolved with water and the reagents of Erio Chrome Cyanine-R method were added to the tube. Then it was completed to 10.0 mL with distilled water. The analyte in the final solution was determined by Erio Chrome Cyanine-R/UV–vis Spectrophotometry standard method in 535 nm [45].

2.4. Application to real samples

2.4.1. Analysis of water samples

10 mL of CRM-TMDW-500 Drinking Water was taken to determine the level of aluminium(III). The real water samples (500 mL) analysed were filtered through a cellulose membrane filter (Millipore) of 0.45 µm pore size. The pHs of the samples were adjusted to 8. Then the separation/preconcentration method given above was applied. The concentration of the investigated analyte ion in the final solution was determined by UV–vis spectrophotometer.

2.4.2. Procedure for analysis of dialysis solution

The dialysis solutions for haemodialysis were collected from a hospital from Trabzon, Turkey. The concentration (g L⁻¹) of each component was as follows.

(A) Concentrated acidic solution for haemodialysis (Diasol, Eczacibasi): NaCl 214.80; KCl 2.612; CaCl₂·2H₂O 7.720; MgCl₂·6H₂O 3.558; CH₃COOH; 4.207.

(B) Concentrated basic solution for haemodialysis (Diasol, Eczacibasi): NaHCO₃ 84.0.

The analysis of haemodialysis concentrate was carried out after dilution 1:20 with the distilled water. 500 mL of diluted dialysis concentrate was neutralised, and then adjusted to pH 8 with NaOH and HNO₃. This solution was analysed using the preconcentration procedure described above. In the final solution aluminium was determined by UV–vis spectrophotometer.

Various amounts of aluminium were also spiked to liquid real samples.

3. Results and discussion

Al³⁺ ions were accumulated on the coprecipitant (Co²⁺/8-HQ) over various mechanisms such as surface adsorption, ion-exchange, surface precipitation, and occlusion, after then the precipitate of Co²⁺/8-HQ, insoluble in water, was formed in pH 8.0.

3.1. Effect of pH

pH of the solutions was adjusted in a range of 1–12 using diluted NaOH and diluted HNO₃ and the present method was applied to this solutions. The results are given in Fig. 1. The percent recoveries in Figs. 1 and 2 were calculated using the equation $(C_x/C_s) \times 100$. In this equation, C_x and C_s are defined as found and added aluminium concentrations, respectively [23]. The highest recoveries for aluminium (III) obtained in the pH range 7–10. After pH 10, the recovery of aluminium(III) decreased with increasing of pH. Because above pH 10, most of Al³⁺ ions change to Al(OH)₄⁻, the coprecipitation efficiency of the method may decrease [45]. The

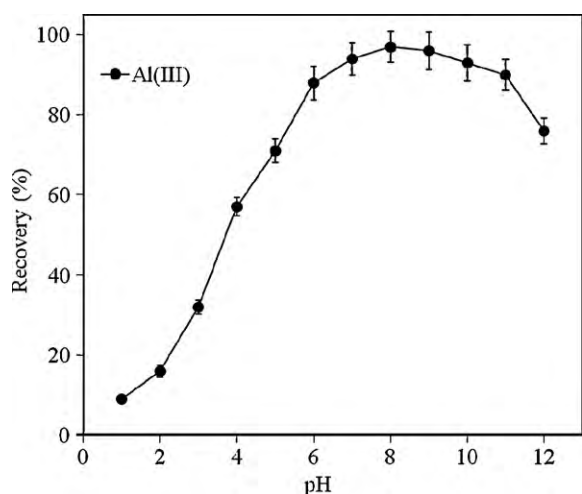


Fig. 1. The pH effects on the recoveries of aluminium(III) (amounts of aluminium(III): 1 μg , amounts of carrier element: 1 mg cobalt(II), amounts of ligand: 5 mg 8-hydroxyquinoline, sample volume: 50 mL, $N=3$).

optimum pH value was selected as pH 8.0 in all subsequent works for separation and pre-concentration of aluminium(III).

3.2. Effects of amount of Co^{2+} as carrier element

The influences of amount of Co^{2+} as carrier element on the recovery of aluminium(III) ion were also investigated. The results are shown in Fig. 2. The recoveries were not quantitative without Co^{2+} . The recovery increased and reach to quantitative value for aluminium(III) at the range of 0.75–1.50 mg of Co^{2+} due to the formation of Co/8-HQ precipitate. Because excess amounts of Co^{2+} ions present in the medium may interfere on Erio Chrome Cyanine-R/UV-vis Spectrophotometry standard method, after 1.50 mg, the recovery of aluminium(III) have been decreased with increasing amount of Co^{2+} . In the light of these results, 1.0 mg of Co^{2+} as carrier was used in all further works.

3.3. Effect of 8-HQ amount

The effect of 8-HQ amount on the present procedure was investigated between 0 and 3.0 mL in the medium containing the constant amount of Co^{2+} (1.0 mg) under optimal conditions. The recoveries of

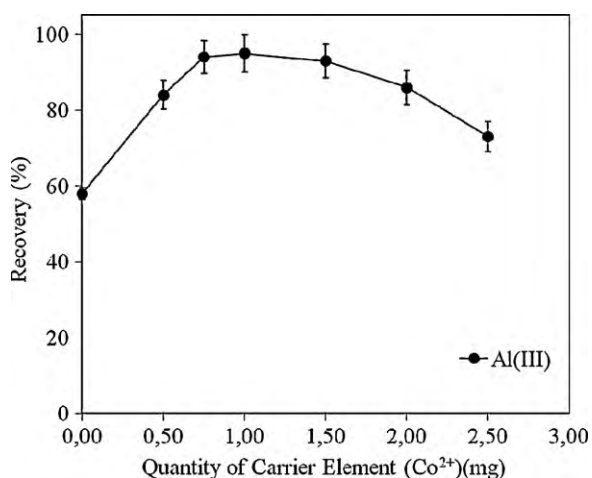


Fig. 2. The influences of amount of Co^{2+} on the recoveries of aluminium ion (pH 8, amounts of aluminium(III): 1 μg , amounts of ligand: 5 mg 8-hydroxyquinoline, sample volume: 50 mL, $N=3$).

aluminium(III) were not quantitative (below 95%) without adding 8-HQ. The recovery of aluminium(III) increased with increasing amount of 8-HQ. The results show that for quantitative recovery of aluminium(III), 8-HQ is necessary. Quantitative recovery value for aluminium(III) was obtained after the addition of 0.6 mL of 8-HQ, so all subsequent works were carried out with 1.0 mL (0.5%, w/v) of 8-HQ (5 mg). Because excess amounts of 8-HQ present in the medium did not form any additional coprecipitant, excess 8-HQ was removed as supernatant after centrifugation. Hence, above 0.6 mL, the recovery of aluminium(III) did not change with increasing amount of 8-HQ.

3.4. Effect of standing time, centrifugation rate and time

The standing time, centrifugation rate and time were also examined on the kept other parameters constant due to formation of precipitate related to these factors and also these parameters effect the quality of coprecipitant. For that purpose 1.0 mL of 8-HQ (0.5% w/v in ethyl alcohol) were added into a series of 50 mL of solutions, containing 1 μg of aluminium (III). Then the standing time was investigated in the range of 0–15 min. After 10 min, quantitative recoveries were obtained so optimum standing time was determined as 10 min for all subsequent works.

The effects of the centrifugation rate were examined in the range of 2000–3500 rpm, under optimal conditions. The optimum centrifugation rate was determined 2750 rpm. And the effects of centrifugation time were investigated on the recoveries of aluminium(III) in the range of 5–25 min at 2750 rpm. After 15 min, quantitative recoveries were obtained so all the other works were performed at 2750 rpm for 15 min.

3.5. Effect of sample volume

The effects of sample volume were examined in range of 50–1000 mL to possible application of the coprecipitation procedure for natural water samples. Because of this point the influences of the sample volume on the recoveries of aluminium(III) were investigated in the sample volume containing 1 μg of aluminium (III) using model solutions. For 50 mL of sample volumes, the precipitates formed in a polyethylene tube and solutions were separated each other with centrifugation. For above 50 mL of sample volumes, the precipitates were filtered through 0.45 μm cellulose nitrate membrane. The result showed that the recovery of aluminium(III) was quantitative up to 500 mL of sample volume. Above 500 mL, the recovery decreased with increasing the sample volume. Because quantity of aluminium used in experiments is low

Table 1

Influences of some foreign ions on the recoveries of aluminium(III) (V: 50 mL, amounts of carrier element: 1 mg cobalt(II), amounts of ligand: 5 mg 8-hydroxyquinoline, final volume: 10 mL, $N=3$).

Ions	Concentration (mg L^{-1})	Recovery (%)
Na^+	10,000	94 \pm 3
K^+	2000	98 \pm 6
Ca^{2+}	2000	97 \pm 5
Mg^{2+}	2000	95 \pm 2
Cl^-	15,000	93 \pm 5
PO_4^{3-}	1000	96 \pm 6
SO_4^{2-}	2000	97 \pm 2
NO_3^-	20,000	94 \pm 5
F^-	250	96 \pm 3
Cr^{3+} , Cd^{2+} , Ni^{2+} , Cu^{2+} , Fe^{3+} , Mn^{2+} , Zn^{2+} , Pb^{2+}	50	99 \pm 5
Mixed ^a		94 \pm 4

^a 15,000 mg L^{-1} Na^+ and Cl^- , 1000 mg L^{-1} Ca^{2+} , Mg^{2+} , K^+ and SO_4^{2-} , 500 mg L^{-1} PO_4^{3-} , 20,000 mg L^{-1} NO_3^- , 100 mg L^{-1} F^- and 10 mg L^{-1} Cr^{3+} , Cd^{2+} , Ni^{2+} , Cu^{2+} , Fe^{3+} , Mn^{2+} , Zn^{2+} and Pb^{2+} .

Table 2
Aluminium(III) determinations in spiked test solutions (V: 50 mL, amounts of carrier element: 1 mg cobalt(II), amounts of ligand: 5 mg 8-hydroxyquinoline, final volume: 10 mL, N: 3).

Sample	Al(III)		
	Added (μg)	Found (μg)	Recovery (%)
Stream water	–	0.98 \pm 0.04	–
	1	1.88 \pm 0.09	95 \pm 5
	5	5.75 \pm 0.22	96 \pm 4
Sea water	–	0.80 \pm 0.05	–
	1	1.69 \pm 0.05	94 \pm 3
	5	5.71 \pm 0.18	98 \pm 3
Tap water	–	0.63 \pm 0.05	–
	1	1.55 \pm 0.04	95 \pm 2
	5	5.48 \pm 0.12	97 \pm 2
Acidic haemodialysis solution ^a	–	BDL ^b	–
	1	0.93 \pm 0.02	93 \pm 2
	5	4.78 \pm 0.15	96 \pm 3
Basic haemodialysis solution ^a	–	BDL	–
	1	0.96 \pm 0.04	96 \pm 4
	5	4.81 \pm 0.22	96 \pm 4

^a The haemodialysis concentrates were used after dilution 1:20 with a de-ionised water.

^b Below detection limit.

(1.0 μg), above 500 mL of sample volumes may cause decreasing of aluminium recovery by reducing the coprecipitation capacity of the method. The preconcentration factor (PF) is calculated by the ratio of the highest sample volume with the analytes under study (500 mL) and the lowest eluent volume (10 mL). The preconcentration factor was 50 [23].

3.6. Effect of diverse ions

The interferic effects of matrix components of real samples especially highly saline samples including seawater, dialysis solution are important problem in the determination of heavy metals. The effect of some foreign ions (Table 1) was examined. A fixed amount of aluminium(III) was taken with different amounts of foreign ions and recommended procedure was followed. Tolerable limit was defined as the highest amount of foreign ions that produced an error not exceeding 5% in the determination of aluminium(III). The results are summarized in Table 1. The results show that large numbers of anions and cations used have no considerable effect on the determination of aluminium(III). Also some transition metals at mg L^{-1} levels were not interfered on the recoveries of aluminium(III). As a result the proposed separation/preconcentration method could be applied to the highly saline samples and the samples that contain some transition metals at tolerable level given in Table 1.

3.7. Analytical figures of merit

The reproducibility of the presented procedure was evaluated by model solution containing 1 μg aluminium(III). The precision of the method was evaluated as the relative standard deviations obtained after replicated analysing samples ($N = 10$). It was found that the recovery of aluminium(III), was 97 ± 4 at 95% confidence level. The relative standard deviations (RSD) of these determinations were below 6%.

The detection limit, defined as the concentration equivalent to three times the standard deviation of 10 replicate measurements of the blank samples, for aluminium(III) was $0.2 \mu\text{g L}^{-1}$ for 50 mL of sample volume and 10.0 mL of final volume. The limit of detection was calculated by dividing the instrumental detection limit by the preconcentration factor.

3.8. Application to real samples

Tests of addition/recovery in the experiments for aluminium were performed in three water samples (sea water, stream water and tap water) and two dialysis solutions (acidic solution for haemodialysis and basic solution for haemodialysis). The results are given in Table 2. A good agreement was obtained between the added and measured aluminium amounts. The percent recoveries in Table 2 were calculated using the equation $m_x / (m_n + m_s) \times 100$. In this equation, m_x , m_n and m_s are defined as quantity of aluminium found after addition of spiked solution in real sample, quantity of aluminium in real sample and quantity of aluminium in spiked solution added to the real sample, respectively [24]. The recovery value for the aluminium ion was greater than 95%. These values were quantitative and it shows that the presented procedure could be applied for the preconcentration of aluminium(III) in real samples. Relative error was lower than 7% for aluminium(III).

The validation of the proposed method was performed by the determination of aluminium(III) using certified reference material (sample volume: 10 mL, $N = 3$), CRM-TMDW-500 Drinking Water containing various elements such as Al^{3+} , Na^+ , Ca^{2+} , Cu^{2+} , Fe^{3+} , Zn^{2+} , Cd^{2+} , Pb^{2+} , Mn^{2+} , Ni^{2+} , Co^{2+} , etc. in 0.5 mol L^{-1} HNO_3 medium. The results revealed good agreement between the observed value ($115.4 \pm 4.7 \mu\text{g L}^{-1}$) and certified value ($120.0 \pm 0.6 \mu\text{g L}^{-1}$) and the recovery was found as 96%. The proposed separation/preconcentration method was also applied to the determination of aluminium in environmental water samples and dialysis solutions. The results are given in Table 3.

Table 3

The level of aluminium(III) in environmental water samples and haemodialysis solutions after application of the presented procedure (sample volume: 500 mL, Amounts of carrier element: 1 mg cobalt(II), Amounts of ligand: 5 mg 8-hydroxyquinoline, final volume: 10 mL, $N = 3$).

Sample	Concentration ($\mu\text{g L}^{-1}$) ^a
Stream water	19.5 \pm 0.9
Sea water	16.0 \pm 0.7
Tap water	12.5 \pm 0.5
Acidic haemodialysis solution ^b	11.2 \pm 0.5
Basic haemodialysis solution ^b	9.3 \pm 0.3

^a Uncertainty at 95% confidence limit.

^b The haemodialysis concentrates were used after dilution 1:20 with a de-ionised water.

Table 4

Comparison of the method with some recent studies on preconcentration of aluminium reported in the literature.

Method	System	Medium pH	LOD	RSD (%)	PF	Detection	Ref.
Solid-phase extraction	Amberlite XAD-1180/ pyrocatechol violet	8.0–9.0	21.0 ng L ⁻¹	<10	150	GFAAS	[23]
On line solid-phase extraction	Controlled pore glass/ L-methionine	12.5	25.0 ng L ⁻¹	2.5	1600	ICP-OES	[2]
Kinetic-spectrophotometry	Nile Blue A/potassium bromate	0.2 mol L ⁻¹ H ₂ SO ₄	34.0 µg L ⁻¹	1.7	–	UV-vis	[19]
On line liquid-liquid extraction	8-hydroxyquinoline/ methylisobutylketone	8.0	0.3 µg L ⁻¹	3	3	GFAAS	[6]
Cloud point extraction	8-Hydroxyquinoline/ Triton X-114	6.2	0.79 µg L ⁻¹	2.7	10	Spectrofluorophotometer	[13]
Cloud point extraction	Morin/1-undecanol	4.5	0.8 µg L ⁻¹	4.5	128	ICP-OES	[28]
Coprecipitation	Co ²⁺ /8-hydroxyquinoline	8.0	0.2 µg L ⁻¹	<6	50	UV-vis	This work

3.9. Comparison of the method with others

The data from the present method have been compared with those of recent reported methods on preconcentration of aluminium (Table 4). 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 using FAAS, Spectrofluorophotometry, GFAAS and UV-vis Spectrophotometry and other methods [19,23,28,46–48]. Other parameter, PF (50) is relatively high enough when compared to some of the others methods. In addition, the cited methods are more complicated and use more reagents than this method, namely application of this method is simpler and takes less time.

4. Conclusion

The coprecipitation method presented is simple, efficient and sensitive preconcentration in environmental samples. Under the optimum experimental conditions, quantitative recoveries were achieved for a preconcentration factor of 50. The recoveries of element in the presence of the most common matrix elements containing the alkaline and alkaline earth metals and transition metals were fairly good. The developed method can be recommended for routine analysis of aluminium ions in the dialysis fluids and natural water samples.

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