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A Rapid Spectrofluorometric Method for the Determination of Aluminum at Nano-trace Levels in Some Real, Environmental, Biological, Hemodialysis, Food, Pharmaceutical, and Soil Samples Using 2′,3,4′,5,7-Pentahydroxyflavone

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A very simple and non-extractive spectrofluorometric method for the swift determination of aluminum at nano-trace levels using 2′,3,4′,5,7-pentahydroxyflavone (morin) has been developed. Morin reacts in a slightly acidic (0.005 – 0.025 M H_2SO_4) solution with aluminum in 20% ethanol to produce a highly fluorescent complex in aqueous solution, which has excitation and emission wavelengths of λ_{ex} = 270 and λ_{em} = 565 nm, respectively. Linear calibration graphs were obtained for 0.01 – 800 μg L^{-1} of Al, providing a detection limit of 1 ng L^{-1}. The limit of quantification of the reaction system was 10 ng L^{-1}. The stoichiometric composition of chelate is 3:2 (Al:morin). The developed method was successfully used in the determination of aluminum in several Standard Reference Materials (SRM) as well as in some water, biological, hemodialysis solutions, food, pharmaceutical, soil sample, and complex synthetic mixtures. The results of the proposed method for biological and food analysis were found to be in excellent agreement with those obtained by AAS. The results of the proposed method for hemodialysis solutions were analogous with those obtained using the method described in British Pharmacopoeia within 95% confidence limits.

Keywords Spectrofluorometry, aluminum-determination, morin, hemodialysis-solutions, environmental, biological, food, pharmaceutical, soil samples

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Introduction

Aluminum has long been believed to be virtually non-toxic and non-absorbable in the gastrointestinal tract. However, current findings revealed that the introduction of Al in the human body can cause many diseases such as anemia,[1] dementia,[2] cardiotoxicity,[3] and gastrointestinal diseases.[4] Al accumulation was recently confirmed in the brain surpassing conventional bone accumulation. As a result, Al accretion leads to Alzheimer's disease,[5] which manifests itself in the senile and presenile ages as central nervous-system degeneration. One of the factors that trigger Alzheimer's disease with a series of disastrous events, is the binding of Al to Ferritin. Ferritin is a protein that binds to Fe and Al. Ferritin is extracted from the brains of individuals suffering from Alzheimer's disease at concentrations of 5 or 6 times larger than those found in healthy individuals.[6]

Hemodialysis is a widely used life-saving treatment for patients worldwide. A water volume ranging from 18000 to 36000 L per year is needed to conduct hemodialysis. If the water is contaminated with enough Al, it directly goes into the bloodstream and accumulates in the bones and brain, causing diseases such as osteomalacy, renal osteodystrophy, and dialysis encephalopathy.[7] Thus, the water quality parameter is set different for dialysis water and conventional drinking water. Hence, the maximum tolerable limit of Al is set 10 μg L^{-1} (RDC No. 11/2014) and 200 μg L^{-1} (Portaria 2914/2011) for dialysis and drinking water respectively according to Brazilian legislation.[8,9] Analytical methodologies capable of quantifying such a low concentration of Al are required in order to maintain the regulatory restrictions set by organizations.

Inductively coupled plasma mass spectrometry (ICP-MS), polarography, graphite furnace atomic absorption spectrometry (GF-AAS), and stripping voltammetry have been used for the determination of trace concentrations of aluminum in water, dialysis fluids, and the serum of patients undergoing hemodialysis because of their accuracy and sufficient detection power to preclude the need for sample preconcentration.[10-12] Moreover, other techniques, such as flame atomic absorption spectrometry (FAAS), inductively coupled plasma optical emission spectrometry (ICP-OES), and visible spectrophotometry, require preconcentration for the determination of aluminum at such trace and ultra-trace levels.[13-15] Direct analytical methods for the determination of aluminum at trace and ultra-trace levels are scarce in the literature. Hence, its accurate determination at trace and ultra-trace levels using a simple and rapid method is of paramount importance.

This study demonstrates a simple unswerving spectrofluorometric method for the ultra-trace determination of aluminum. The method holds discrete advantages over current approaches with respect to several aspects of the analytical parameters.

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The method is based on the formation of a fluorescence complex of Al and morin (2′,3,4′,5,7-pentahydroxyflavone) in a slightly acidic (0.005 – 0.025 M H_2SO_4) solution in the presence of ethanol. The complex gives excellent fluorescence signals for the direct determination of Al. The reagent blank did not show a significant fluorescence intensity. The method's selectivity was tested with a suitable masking agent in some complex mixtures.

Experimental

Apparatus

A Shimadzu (Kyoto, Japan) (Model-RF-5301PC) spectrofluorometer and a Jenway (England) (Model-3010) pH meter were used for obtaining a fluorescence intensity and pH, respectively. The infrared spectrum was recorded with a Shimadzu, Model-IR Prestige 21, FTIR spectrometer with a DTGS KBr detector. A Thermo Fisher Scientific (Model-iCE 3000, origin USA) atomic absorption spectrophotometer equipped with a microcomputer-controlled nitrous oxide-acetylene flame and a Shimadzu (Kyoto, Japan) (Model-9800) inductively coupled plasma–optical emission spectrometer (ICP-OES), [λ = 418 nm, plasma gas flow rate (L min^{-1}) = 15, LOD: 1 μg L^{-1} of V, RF power (W) = 1400, nebulizer gas flow rate (L min^{-1}) = 1 – 10] were used to compare the results.

Reagents and solutions

Analytical-grade reagents were all used throughout. The reagent solution was prepared by dissolving the requisite amount (0.0013 g) of morin (BDH chemicals, pro analysis grade, 99.5%) in a known volume (25 mL) of ethanol. A freshly prepared reagent (morin) solution (10^{-5} M) was used whenever required. Melting point and FTIR spectroscopy were used to check the purity of morin. The melting point of the reagent (morin) was 300 ± 2°C (lit. 300 – 303°C)[16]. The FTIR spectrum is shown in Supporting Information (Fig. S1). The presence of a peak at 1625.35 cm^{-1} was due to the characteristic C=O double-bond peak ($\nu^{C=O}$, 1612 – 1630 cm^{-1}) and the peak at 1560.25 cm^{-1} was due to the characteristic C=C double-bond peak ($\nu^{C=C}$, 1527 – 1591 cm^{-1}). The peak at 1285.52 cm^{-1} was due to the characteristic C=O double-bond peak ($\nu^{C=O}$, 1260 – 1326 cm^{-1}) of the morin. The trivalent aluminum solution was prepared from aluminum sulfate ($Al_2(SO_4)_3{\cdot}18H_2O$) (Aldrich A.C.S. grade) in deionized water and standardized by ethylenediaminetetraacetic acid (EDTA) using a xylenol orange indicator during the titration.[17] Solutions of inorganic ions and complexing agents were prepared from their AnalaR grade or equivalent-grade water-soluble salts (or the oxides and carbonates in hydrochloric acid). Niobium, tantalum, titanium, zirconium, and hafnium solutions were from their corresponding oxides (Specpure, Johnson Matthey), recommended by Mukharjee.[18] Special treatment was done for insoluble substances.[19]

Procedure

To 0.1 – 1.0 mL of a neutral aqueous solution containing 0.1 – 8000 ng of aluminum in a 10-mL calibrated flask was mixed with a 1:70 – 1:300 fold molar excess (preferably 1 mL of 10^{-4} M) of the morin solution, trailed by the mixing of 0.5 – 2.5 mL (preferably 1 mL) of 0.01 M of H_2SO_4. The solution was mixed well and allowed to stand for 5 min, after which 2 mL of absolute ethanol was added and the mixture was diluted up to the mark with doubly distilled deionized water. The fluorescence intensity of the system was measured at 565 nm against a corresponding reagent blank, prepared concurrently, while keeping the excitation wavelength maximum at 270 nm and the instrument setting the same. The aluminum content in an unknown sample was determined using a concurrently prepared calibration graph.

Sample collection and preservation

Water samples were collected in polythene bottles from different places of Bangladesh. After collection, HNO_3 (1 mL L^{-1}) was added as a preservative. Blood and urine samples were collected in polythene bottles from affected persons of Chittagong Medical College Hospital, Bangladesh. Samples were collected upon taking the consent of the patient and also with the permission of a doctor. Hemodialysis solutions were collected in polythene bottles from affected persons of Chittagong Medical College Hospital, Bangladesh. After collection, HNO_3 (1 mL L^{-1}) was added as a preservative. Food samples (cake, cookies, coffee, noodles, egg, baking powder, rice, and wheat powder) were collected from the local market of Chittagong. Samples (coffee, rice, cookies, and noodles) were used as dry conditions and homogenized with a ceramic mortar. Pharmaceutical samples (antacid tablets) of different companies were collected from a local pharmacy of Chittagong. Soil samples were from several places of Bangladesh. Samples were dried in air and homogenized with a mortar.

Results and Discussion

Spectral characteristics

The excitation and emission spectra of the fluorescent Al-morin complex in 0.01 M sulfuric acid medium were recorded using a spectrofluorometer. The excitation and emission maxima were at 270 and 565 nm, respectively. The reagent blank displayed an insignificant fluorescence signal, regardless of having a wavelength maximum in a similar section. The chemical structure of the reagent is shown in Fig. 1. In all instances, measurements were made against the reagent blank. The fluorescence spectra are shown in Fig. 2. The fluorescence intensity is highly machine-dependent, and changes based on the condition of the measurement. Thus, the whole method has been optimized for gaining higher fluorescence intensity value.[20] For example, the change in the excitation and emission slit changes the fluorescence intensity of the machine. Thus, for every case, the condition of measurement should be identical for both the sample and reagent blanks. For any subsequent measurement, the fluorescence intensity value of the reagent blank is always subtracted from every sample measurement.

Optimization of some parameters on the fluorescence intensity

Effect of solvent. Because morin is poorly soluble in water, an organic solvent was used for the system. Of the various solvents [chloroform, benzene, carbon tetrachloride, n-butanol, isobutanol, ethanol, 1,4-dioxane and *N*,*N*-dimethylformamide (DMF)] studied for the system, ethanol was finest for it. Hence, several concentrations of the solvent were tested and no drastic effect was observed on the fluorescent intensity. It was detected that the Al-morin system with 10 μg L^{-1} of Al in absolute ethanol solution produced a constant fluorescence intensity, as shown in Fig. S2 (SI). A concentration of 20% v/v ethanol in the final volume was enough to prevent any precipitation or turbidity. Therefore, a 20% v/v ethanolic solution was used in the recommended procedure.

Effect of acidity and reagent concentration. Of the various acids (nitric, sulfuric, hydrochloric, and phosphoric) studied, sulfuric acid was found to be best for the system.

The fluorescence intensity plateaued when 10 mL of a solution (10 μg L^{-1} of Al) contained 0.5 – 2.5 mL of 0.01 M sulfuric acid at room temperature (25 ± 5°C). Outside this range of acidity, the fluorescence intensity decreased (Fig. 3A). The optimum acidity range in the final solution is, therefore, 0.005 – 0.025 M H_2SO_4. For all subsequent measurements, 1 mL of 0.01 M sulfuric acid was added. Different molar excesses of morin were added to a fixed metal ion concentration, and the fluorescence intensities were measured according to the standard procedure. It was observed that at 10 μg L^{-1} Al metal and the reagent molar ratios of 1:70 – 1:300 produced a constant fluorescence intensity of the complex. Outside this range of reagents, the fluorescence intensity decreased (Fig. 3B). At different aluminum concentrations (0.5 and 1 μg L^{-1}), the effect of varying the reagent concentration was similar. For all subsequent measurements, 1 mL of 1×10^{-4} M morin reagent was added.

Effect of temperature and time. The Al-morin system attained the maximum and constant fluorescence intensity at 15 – 40°C temperature. Hence, all experiments were done at room temperature (25 ± 5°C). On the other hand, the reaction is instantaneous. The Al-morin system attained the maximum and constant fluorescence intensity immediately (within 5 min) after dilution of the solution to the final volume, which then remained strictly unaltered for 24 h at room temperature (25 ± 5°C).

Calibration graph (Beer's law and sensitivity). The well-known equation for spectrofluorimetric analysis in very dilute solutions derived from Beer's law. The effect of the metal concentration was studied over 0.001 – 1200 μg L^{-1} distributed in six different sets (0.001 – 0.01, 0.01 – 0.1, 0.1 – 1, 1 – 10, 10 – 100, and 100 – 1200 μg L^{-1}) for convenience of the measurement. The fluorescence intensity was linear over a wide range (10 pg mL^{-1} to 800 ng mL^{-1} for 0.01 – 800 μg L^{-1} of aluminum at an excitation wavelength of 270 nm and emission wavelength of 565 nm, representing five linear graphs (0.01 – 0.1, 0.1 – 1.0, 1 – 10, 10 – 100 and 100 – 800 μg L^{-1}). Of five calibration graphs, the one showing the limit of the linearity range is shown in Fig. 4. The limit of detection and the limit of quantitation

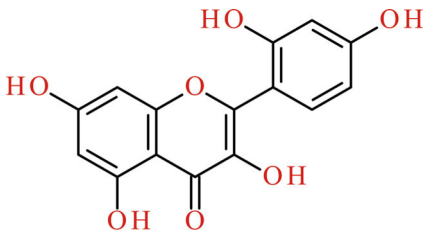

Fig. 1 Structure of 2′,3,4′,5,7-pentahydroxyflavone (morin).

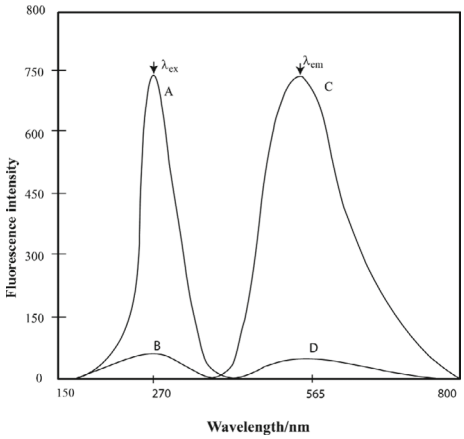

Fig. 2 A and B, Excitation spectra of the Al-morin system and reagent blank, respectively (λ_{ex} = 270); C and D are the corresponding emission spectra (λ_{em} = 565).

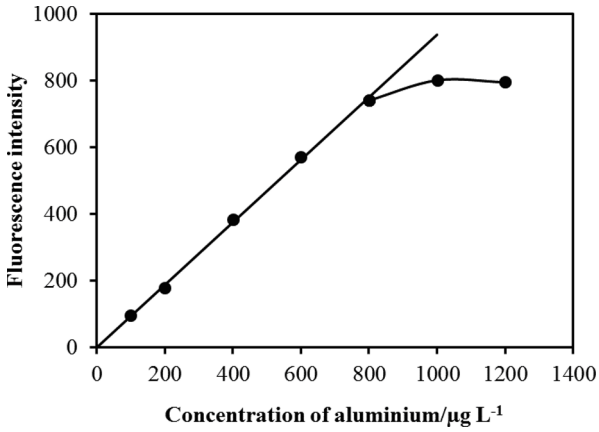

Fig. 4 Calibration graph of aluminum; bandwidth; Ex. Slit-3; Em. Slit-1.5.

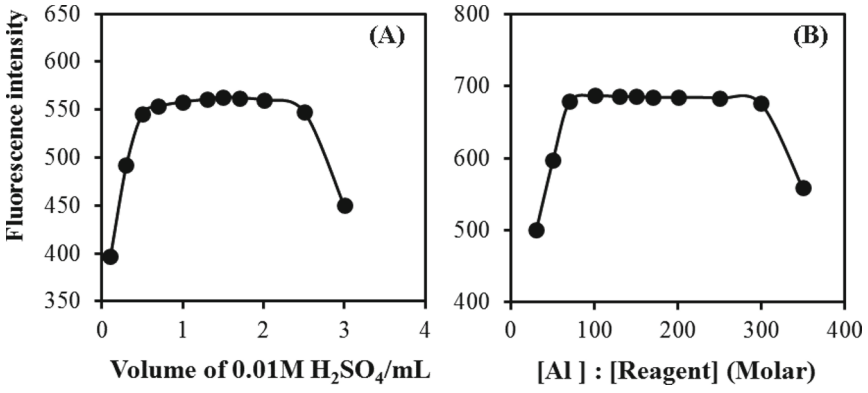

Fig. 3 Effect of the acidity (H_2SO_4) and reagent (Al:morin molar concentration) on the fluorescence of the Al-morin system.

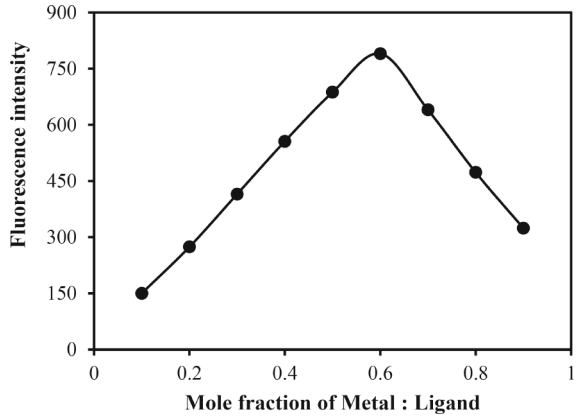

Fig. 5 Job's method for determining the composition of an Al:morin (3:2) complex.

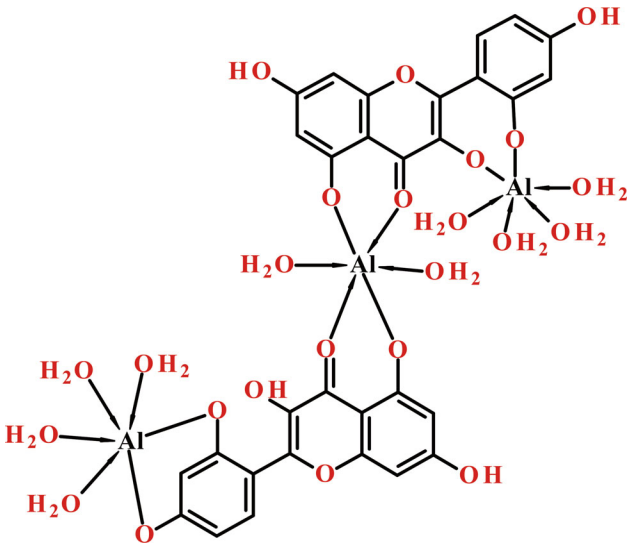

Fig. 6 Probable structure of the [Al_3(2′,3,4′,5,7-pentahydroxyflavone)$_2$] complex.

were found to be 1 ng L^{-1} and 10 ng L^{-1}, respectively. The selected analytical parameters obtained with the optimization experiments are summarized in (Table S1, SI).

Effect of foreign ions. Several ions and complexing agents were considered independently to examine their effect on the quantification of 1 µg L^{-1} of aluminum. A fixed criterion was set for the interference study, which was a ±5% deviation from the anticipated result of only Al. The results are summarized in Table S2 (SI). The formulae for calculating the tolerance ratio is:

$$(X - Y)/Y \times 100\%.$$

Here, X is the fluorescence signal for 1 µg L^{-1} Al with varying amounts of species (x). Y is the fluorescence signal of 1 µg L^{-1} standard Al. Briefly, 1 µg L^{-1} standard Al was mixed with varying amounts of potentially interfering species, and the tolerance limit was calculated from the formulae above. If the value was found outside the range (95 – 105)% which is a ±5% deviation from the standard Al signal, then that amount of species was taken as interfering the signal. After that ratio of that weight of interfering species and 1 µg of Al is termed as its tolerance ratio.

Very few interferences were observed for a large number of ions. The serious interferences were from Cd(II) and Fe(II) ions. Masking agents allowed us to get a higher tolerance limit for the interfering ions. For Cd(II) and Fe(II) ions, EDTA and tartrate were utilized as masking agents, respectively. A 50- and 100-fold excess of Cd(II) and Fe(II) ions could be masked with EDTA and tartrate, respectively. These two ions were masked because Cd(II) and Fe(II) would probably form complexes with EDTA and tartrate, respectively. Centrifugation and filtration were employed in the case that any precipitation occurred during the masking process. The amount mentioned in the actual amount studied instead of indicating the tolerance limit.

Composition of the fluorescent complex (stoichiometry of the complex). The Job's method[21] of continuous variation and the molar-ratio method[22] were applied to ascertain the stoichiometric composition of the complex under the optimum conditions. An Al-morin 3:2 complex was indicated by both methods. Experimental data are shown graphically in Fig. 5. Referring to this data, it can be concluded that the complex formed in a 20% ethanolic aqueous medium, is in the form of [Al_3(2′,3,4′,5,7-pentahydroxyflavone)$_2$]. The probable structure is shown in Fig. 6.

The complex formed in this study is unique, since it has a lot of advantages over other fluorescent Al-complexes. A study by Yıldız *et al.* based on complex formation with 3′,6′-bis-(diethylamino)-2-{[(1*E*)-(4-ethoxyphenyl)methylene]amino}spiro-[isoindole-1,9′-xanthen]-3(2*H*)-one with aluminum was found to have a wide range of aluminum determination (0 – 1000 mg L^{-1}), but had a detection limit of 3.02 µg L^{-1}.[23] On the other hand, a similar detection limit with our study was gained by Mánuel-Vez *et al.* but had a comparatively narrower detection range.[24] The present study has one of the lowest detection limits among other methods. Moreover, the lower limit of the detection range was very low in this method, which is very vital for a real sample determination without preconcentration. The complex formation was quick, and the measurement could be done instantaneously. Thus, this method has an excellent benefit to be used in several real sample analyses for aluminum determination. A number of other fluorescent aluminum complexes have been tabulated with their detection limit, the range of aluminum determination is compared with this study in Table 1.

Application of the proposed method

Synthetic mixtures and certified reference materials. Several synthetic mixtures of varying compositions containing aluminum and diverse ions of known concentrations were determined by the present method using EDTA as a masking agent.[25] The results were found to be highly reproducible, as shown in Table S3 (SI). Accurate recoveries were achieved in all solutions. The proposed procedure for the spectrofluorimetric determination of aluminum was applied to the analysis of estuarine sediment (CRM-397), hemodialysis solution (SIF-BP 466A), freshwater (NIST-CRM 1640a), bovine liver (NIST-SRM 1577a), human urine (normal) (NIST-SRM 2670), human hair (NIES-CRM 5). CRMs obtained from The National Research Council of Canada and analyzed using EDTA or tartrate as a masking agent.[26] Based on five replicate analyses, the average aluminum concentration determined by the spectrofluorimetric method was in excellent agreement with the certified values. The results are given in Table 2.

Environmental soil and water. Surface soil from several parts of Chittagong was measured using the proposed method, and the results are summarized in Table S4 (SI). The results of analyses

Table 1 Comparison of different Al complexes with the present study

Complexing agent	Detection limit	Linear range	Solvent	Reference
2′,3,4′,5,7-Pentahydroxyflavone.	10 ng L^{-1}	0.01 – 800 μg L^{-1}	MeOH	This study
3′,6′-Bis(diethylamino)-2-{[(1*E*)-(4-ethoxyphenyl)methylene]-amino}spiro[isoindole-1,9′-xanthen]-3(2*H*)-one	3.02 μg L^{-1}	0 – 1000 mg L^{-1}	EtOH	23
Salicylaldehyde picolinoylhydrazone (SAPH)	9.8 ng L^{-1}	1 – 25.1 μg L^{-1}	EtOH	24
2-Hydroxy-1-naphthylidene-(8-aminoquinoline)	3.4 μg L^{-1}	0.05 – 1 mg L^{-1}	MeOH-H_2O	30
N,*N*′-Disalicylidene-1,3-diamino-2-hydroxypropane	0.27 μg L^{-1}	0 – 26.0 μg L^{-1}	Dioxan-H_2O	31
Sodium morin-5-sulfonate and poly(vinyl chloride)	10.99 μg L^{-1}	14.13 μg L^{-1} – 1.62 mg L^{-1}	THF	32

Table 2 Determination of aluminum in certified reference materials

No.	Certified reference materials (Composition, %)	Aluminum, %		
		In CRM	Found (n = 5)	RSD[a]
1	Bureau of Analysed Samples Ltd. No. BAS-10g: High tensile steel (Cu = 60.8; Sn = 0.21; Zn = 30.0; Al = 3.34; Pb = 0.023; Ni = 0.16; Fe = 1.56; Mn = 1.36)	3.34	3.33 ± 0.005	1.5
2	BAS-CRM-20b: Al-alloy (Al = 90.5; Mg = 1.6; Cu = 4.1; Ni = 1.9; Fe = 0.43; Mn = 0.19; Si = 0.24)	90.50	90.48 ± 0.008	1.0
3	BAS-CRM-32a: Al-bronze alloy (Cu = 85.9; Zn = 0.94; Mn = 0.27; Fe = 2.67; Al = 8.8; Ni = 1.16)	8.8	8.75 ± 0.009	2.0
4	GSBD-33001.4-94[b]: High tensile steel (Fe = 12.56; Si = 3.56; Al = 13.12; Ca = 0.17; Mg = 9.97; Cu = 50.95)	13.12	13.15 ± 0.01	2.5
5	SIF-BP 466A[c]: Hemodialysis solution (NaCl = 5.67; $CaCl_2{\cdot}2H_2O$ = 0.26; $MgCl_2{\cdot}6H_2O$ = 0.07; sodium lactate = 3.92; glucose monohydrate = 16.50)	9.0[c]	9.0 ± 0.05	2.0
6	CRM-397: Estuarine sediment	2.297	2.285 ± 0.005	1.8
7	NIST-SRM 1640a: Fresh water[d]	52.6 ± 1.8	52.1 ± 2.0	3.0
8	NIST-SRM 1577a: Bovine liver[e]	2.0	2.05 ± 0.008	1.6
9	NIST-SRM 2670: Urine (normal)[d]	180 ± 0.5	179 ± 0.8	1.5
10	NIES-CRM 5: Human hair[e]	240 ± 1.5	238 ± 2.0	2.5

a. The measure of precision is the relative standard deviation (RSD). b. This CRM was from Beijing NCS Analytical Instruments Co. Ltd. China. c. Values in ng mL^{-1}. d. Values in μg g^{-1}. e. Values in mg kg^{-1}.

of environmental water samples from various sources for aluminum are given in Table S5 (SI). Most spectrofluorimetric methods for the determination of aluminum in natural and seawater require preconcentration or standard addition of aluminum.[27] The concentration of aluminum in natural water and seawater is a few μg L^{-1} in developed countries.[28] The mean concentration of aluminum found in Germany (Western region) drinking water is greater than 10 μg L^{-1}. This method allowed us to measure water samples without any pretreatment.

Biological samples and hemodialysis solutions. The digestion of human blood, urine, human gall stone, and hair sample was done in the presence of oxidizing agents according to a method recommended by Stahr.[29] The results of biological samples and hemodialysis analyses were found to be in excellent agreement with those obtained by AAS. The results are shown in Table 3. The abnormally high value for cancer (Leukemia) patients is probably due to the involvement of a high aluminum concentration with Cu and Zn. In addition, with the method described in British Pharmacopoeia, the determination of aluminum was made using the standard addition method. In order to control the validity of the method, aluminum was detected in the same solutions using the method described in British Pharmacopoeia. The results of the method described in British Pharmacopoeia and the results of this proposed method in diluted hemodialysis solutions are in correlation with each other with 95% confidence limits (Table 4). For the statistical comparison of the accuracy of the proposed method with the accepted standard and routinely used method described in the British Pharmacopoeia, F-test was used. As a result, the proposed method can be used with good accuracy and precision for the routine determination of aluminum in diluted hemodialysis solutions.

Food and pharmaceuticals. The food samples used were baking powder, wheat powder, coffee, rice, egg, noodles, cake, and cookies and these were used under dry conditions. The results of food analyses were found to be in excellent agreement with those obtained by AAS. The results are shown in Table 5. The results of some pharmaceutical analyses were also in excellent agreement with the reported values. The analyses of pharmaceutical samples from several pharmaceutical companies for aluminum are given in Supporting Information (Table S6).

Conclusion

A new rapid, ultra-sensitive, highly selective, and inexpensive spectrofluorometric method with the aluminum-morin system was developed to establish the ultra-trace levels of aluminum in different samples matrices. The proposed method has several remarkable analytical characteristics. It is highly sensitive that the amount of ng L^{-1} of aluminum can be determined without preconcentration in diluted hemodialysis solutions. The low detection limit, 1 ng L^{-1} levels can be measured without preconcentration or the standard addition method. The reaction of aluminum with morin was to be found instantaneous. With suitable masking agents, the reaction can be made highly selective and have better reproducibility (s_r = 0.1%). Therefore, this method can be successfully used in the routine analysis of trace amounts of aluminum in real, environmental, biological, diluted hemodialysis solutions, food, pharmaceutical, and soil samples.

Table 3 Determination of aluminum for blood, urine, human gall stone, and hemodialysis solution

No.	Sample	Aluminum/μg L^{-1}				Sample source[a]
		AAS (n = 5)		Proposed method (n = 5)		
		Found	RSD, %	Found	RSD, %	
1	Blood	150.0 ± 1.0	1.8	153.0 ± 0.8	2.0	Normal adult
	Urine	40.5 ± 0.8	1.0	42.8 ± 1.0	1.5	(Male)
2	Blood	370.0 ± 1.5	2.0	375.0 ± 1.0	1.5	Cancer patient,
	Urine	95.5 ± 1.0	1.5	98.0 ± 0.8	1.0	leukemia (Female)
3	Blood	445.0 ± 2.0	3.0	450.5 ± 1.5	2.5	Lung cancer
	Urine	112.3 ± 1.5	2.0	115.6 ± 1.3	1.8	(Male)
4	Blood	292.0 ± 1.0	1.3	295.0 ± 1.3	1.8	Neuretic patient
	Urine	75.0 ± 0.8	1.5	78.5 ± 1.5	2.0	(Female)
5	Blood	223.0 ± 1.5	2.0	225.5 ± 1.6	2.5	Kidney disease
	Urine	56.8 ± 1.0	1.8	58.8 ± 1.9	2.3	(Male)
6	Human gall stone	45.5 ± 1.2	1.5	47.8 ± 1.8	2.0	Patient (Male)
7	Hemodialysis solutions:	16.0 ± 0.8	1.0	16.8 ± 1.0	1.3	Chittagong medical
	before and after dialysis	250.5 ± 1.5	2.0	255.0 ± 1.5	2.5	college hospital
8	Human hair	255.0 ± 1.8	2.5	260.8 ± 1.5	2.5	Human hair (Male)

a. Samples were from Chittagong Medical College Hospital (with the prior permission of the authority).

Table 4 Comparison for the determination of aluminum in hemodialysis solutions

Parameter	A	B
Mean values of aluminum (before dialysis)	1.58 ± 0.10[a]	1.68 ± 0.09[a]
Standard deviation (s)	0.09	0.08
Relative standard deviation	5.0	3.0
Variance $(s)^2$	6.4×10^{-3}	4.48×10^{-3}
Reproducibility (s_r)	0.31	0.22

A, British Pharmacopoeia method; B, proposed method.
a. Values in ng mL^{-1}.

Table 5 Determination of aluminum in some food samples

No.	Sample	Aluminum/mg kg^{-1} Found[a] ± s			
		ICP-OES		Proposed method	
		Found	RSD[b]	Found	RSD[b]
1	Baking powder	180 ± 1.0	1.8	182.5 ± 1.5	2.5
2	Coffee (*Coffea arabica*)	15.0 ± 0.8	1.5	15.8 ± 1.2	1.8
3	Wheat powder (*Triticum aestivum*)	20.5 ± 1.5	3.0	21.8 ± 1.5	2.5
4	Rice (*Oryza sativa*)	12.0 ± 1.2	1.8	13.5 ± 1.5	2.0
5	Chocolate cake	48.0 ± 1.8	3.2	49.8 ± 2.0	3.0
6	Salten cookies	17.0 ± 1.7	1.9	18.5 ± 1.8	2.5
7	Egg (*Gallus domesticus*)	30.0 ± 2.0	3.0	32.0 ± 2.0	3.5
8	Imported noodles	25.0 ± 2.0	2.8	26.5 ± 1.8	2.5

a. Average of five replicate analyses of each sample.
b. The measure of precision is the relative standard deviation (RSD).

Supporting Information

This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

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