A Simple Spectrophotometric Method for the Determination of Aluminum in Some Environmental, Biological, Soil and Pharmaceutical Samples Using 2-Hydroxynaphthaldehydebenzoylhydrazone

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Abstract

A simple ultra-trace, and highly selective non-extractive spectrophotometric method is presented for the rapid determination of aluminum at trace levels using 2-hydroxynaphthaldehydebenzoyl-hydrazone (HNPBH) as a new spectrophotometric reagent (λ_{max} = 412 nm) in slightly acidic solution (1.5×10^{-5}-1.25×10^{-4} mol L^{-1} H_2SO_4) in 50% N,N-dimethylformamide (DMF) medium. The reaction is instantaneous and absorbance remains stable for over 24 h. The color system obeys Beer's law from 0.01-2.0 mg L^{-1} having detection limit of 1 µg L^{-1} and RSD 0-2%. The average molar absorptivity and Sandell's sensitivity were found to be 2.21×10^4 L mol^{-1} cm^{-1} and 6 ng cm^{-2}, respectively. The stoichiometric composition of the chelate is 2:3. The interference from over 50 cations, anions, and complexing agents (tartrate, oxalate, citrate, EDTA, DMG, 1.10 phenanthrolin, oxine, phosphate, thio-urea, SCN^-) has been studied at 1 mg L^{-1} of Al. The method was successfully applied to some certified reference materials (alloys and steels), environmental waters (inland and surface), biological samples (human blood, urine and gallstone), soils, pharmaceutical samples (entacyd and almasil) and complex synthetic mixtures. The method has high precision and accuracy (s = ±0.01 for 0.5 mg L^{-1}).

1. Introduction

Aluminum is a versatile metal, which has tremendous usage in the realm of industries and other spheres of life. Our earth is a storehouse of this metal in abundance and it is used in every walk of life like engineering, making artificial gems and many other things. Today, this cost-effective metal is widely available throughout the world and its alloys are used extensively for adding strength and utility [1]. Aluminum also used for dialysis dementia [2]. High amount of aluminum is toxic for human [3]. On the other hand, micronutrient roles of the metal ion are also well recognized. Aluminum also found in over the counter medicinal, such as antacids and buffered aspirin, is used as a food additive, and is found in a number of topically applied consumer products such as antiperspirants, and first aid antibiotic and antiseptics [4]. All this findings cause alarming concern in public health, demanding accurate determination of this metal ion at traces and sub-trace levels.

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Spectrophotometry is an essential trace analysis technique and is one of the most powerful tools in chemical analysis. Recently several published spectrophotometric methods [5-29] based on use of various reagents are reported for the determination and detection of Al. Some of these methods are not sensitive, some are suffer from interference, some have limited application, some methods use surfactant, some are solvent extractive, and there are also some methods where they used buffer solution and chelate stabilizer. Some are very lengthy process, time consuming and, pH and temperature dependent. A comparison of few selected process; their spectral characteristics and draw backs are enumerated in Table 1. The shiff-base reagents had widely been applied for the determination of noble metal ions, this type of reagents higher sensitivity and selectivity [30]. In the search for more sensitive shiff-base reagent, in this work, a new reagent 2-hydroxynaphthaldehydebenzoylhydrazone(HNPBH) was synthesized according to the method Sacooni [31] and Salam [32] and color reaction of HNPBH with Al in aqueous media was carefully studied. This paper reports on the use of HNPBH in a very sensitive and highly selective spectrophotometric method for the trace determination of aluminum. This method possesses distinct advantages over existing methods with respect to sensitivity, selectivity, range of determination, simplicity, speed, acidity range, thermal stability, accuracy, and ease operation. The method is based on the selective reaction of the non-absorbent reagent HNPBH, in slightly acidic medium (1.5×10^{-5}-1.25×10^{-4} M H_2SO_4) with Al to produce a greenish chelate, followed by direct measurement of the absorbance in 50% DMF solution. With suitable masking, the reaction can be made highly selective.

2. Experimental Section

2.1. Apparatus

A GBC (Model-Cintra-6) with cintral-2.2 software version double beam UV/visible recording spectrophotometer (Australian) and A Combo pH and EC meter (Model no. HI-98129-water proof) by Hanna were used for measurements of absorbance and pH, respectively. Biological samples were analyzed for trace amounts of Al by a Shimadzu Model No.-AA-640 IF atomic absorption spectrophotometer at 309.3 nm, using a nitrous oxide-acetylene flame for comparison of the results. Infrared spectrum recoded with an FTIR spectrophotometer (Model No-Nicolet5700; Detector-DTGS KBr smart accessory ID-012-593; Beamsplitter-XT-KBr) in the range of 4000-500 cm^{-1}.

2.2. Synthesis and Characterization of The Reagent

The reagent was synthesized in our laboratory according to the method of Sacconi [31] and Salam [32]. The reagent 2-hydroxynaphthaldehydebenzoylhydrazone (HNPBH) was synthesized by two steps. First, benzoylhydrazine (BH) was prepared by refluxing ethylbenzoate (700 mmol) with hydrazine hydrate (700 mmol) at 140°C for 20 hours in a round bottle flux equipped with a condenser and then recrystallized twice from ethanol. An off-white crystalline product was obtained whose melting point was 115°C (Lit. 113-117°C [31]). The reagent was characterized by taking melting point, elemental analysis, and FTIR spectrum and thermogravimetric analysis. The melting point of the reagent was 204°C (Lit. 206°C [31]).

Table 1. Comparison between present and existing spectrophotometric methods for the determination of aluminum.

Reagent	Solvent	Medium Aqueous/ Surfactant/ Organic	Acidity / pH	λ_{max} (nm)	Molar absorption co-efficient ($Lmol^{-1}cm^{-1}$)	Beer's Law (mgL^{-1})	Detection Limit (μgL^{-1})	RSD %	Interference	Remarks
Methylthymolblue [21]	Polyurethane(PU) foam	Extraction	pH 1.5-4.7	528	1.32×10^3	0.15-1	7	0.7	Cr^{6+}, PO_4^{3-}	Solvent extractive Less selective Less sensitive pH dependent
Morin [22]	50% ethanol	Ethanolic medium	Acidity 0.01-0.5 mol L^{-1} H_2SO_4	421	5.3×10^3	0.05-5	10	5	Cd, Fe^{2+}	Less sensitive Less selective Lengthy
Chrome azurol S [23]	Solid phase	Extraction	pH 5.5	615 and 800	2.4×10^3	0.6-4	100	2.1	Many	Lengthy & time consuming Less selective Less sensitive Double λ_{max}
5,8-dihydroxy-1,4-naphthoquinone [24]	50% surfactant	Non-ionic surfactant	pH 4.7	598	1.04×10^4	0.01-1.08	60	5	Cu^{2+}, Cr^{6+}, Fe^{3+}	Less selective Less sensitive pH dependent
2,3,7-trihydroxy-9-[4-(2,4-dihydroxy)phenylazo] phenylfluorone (ARPF) [25]	DMF & acetic acid mixture	Aqueous	pH-6.5	562	1.10×10^4	0-2.2	50	3	Many	Less selective pH dependent Less sensitive
Alizarin red S [26]	Polyvinylpyrrolidone	Acetate buffered	pH-4.75	510	1.7×10^3	0.1-10	40	2	Bi^{3+}, Cu^{2+}, Fe^{3+}	Less selective due to much interference Less sensitive pH dependent
2-hydroxynaphth-aldehydebenzoylhydrazone (HNPBH) **(present method)**	50% DMF	Aqueous	Acidity 1.5×10^{-5}-1.25×10^{-4} mol L^{-1} H_2SO_4	412	2.21×10^4	0.01-2	1	0-2	Nil*	Ultra sensitive Highly selective Aqueous reaction medium. Very simple & rapid Non-extractive

*Using suitable masking agents, the reaction can be made highly selective.

2.3. Reagents and Solutions

All the chemicals used were of analytical reagent grade of the highest purity available.

High-purity DMF (N,N-Dimethylformamide) and high-purity de-ionized water, which are non-absorbent under UV radiation, were used throughout. High-purity water was obtained by passing tap water through a cellulose absorbent and to mixed-bed ion exchange columns, followed by distillation in a corning AG-11 unit. The Al level in the high-purity water was found to be below the spectrophotometric detection limit (3s of the blank) of 1 μg L^{-1}. Glass vessel were cleaned by soaking in acidified solutions of $KMnO_4$ or $K_2Cr_2O_7$ followed by washing with concentrated HNO_3 and rinsed several times with high purity de-ionized water. Environmental water sample (1000 mL each) was kept in polypropylene bottles containing 1 mL conc. HNO_3.

2.4. HNPBH Solution

HNPBH (3.44×10^{-3} mol L^{-1}) solution was prepared by dissolving the requisite amount of HNPBH in known volume of DMF. More dilute solution of the reagent was prepared as required.

2.5. Aluminum Standard Solution

A 100-mL stock solution (1 mg mL^{-1}) (3.71×10^{-2} mol L^{-1}) of Al was prepared by dissolving 895.03 mg of $AlCl_3.6H_2O$ (Merck analytical grade) in deionized water. Aliquots of this solution were standardized with EDTA titration. Working standard solutions were prepared after suitable dilutions of the stock solution.

2.5. General Procedure

To (0.1-1.0) mL of a neutral aqueous solution containing 0.1-20 μg of aluminum in a 10 mL calibrated volumetric flask was added with 70-280 fold molar excess (preferable 1 mL of 3.44×10^{-3} mol L^{-1}) of the HNPBH reagent solution followed by the addition of 0.3-2.5 mL (preferable 1 mL) of 0.0005 mol L^{-1} sulfuric acid. The solution was mixed well and allowed to stand for 1 min; after which 5-mL of N,N-Dimethylformamide was added. The mixture was diluted up to the required volume with deionized water. The absorbance was measured at 412 nm against a corresponding reagent blank. The aluminum content in an unknown sample was determined using a concurrently prepared calibration graph.

3. Results and Discussion

3.1. Development of the Method

3.1.1. Spectra Characteristics

The absorption spectra of Al^{3+}-HNPBH system in aqueous medium in the presence of 1 mL 0.0005 mol L^{-1} H_2SO_4 solution were recorded using the spectrophotometer. The absorption spectra of Al-HNPBH as a symmetric curve with maximum absorbance at 412 nm and an average molar absoptivity 2.21×10^4 L mol^{-1} cm^{-1} is shown in Fig. 2. The reagent blank exhibited negligible absorbance despite having a wavelength at 412 nm.
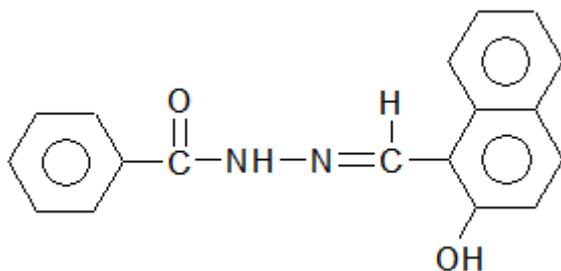
Fig.1. 2-hydroxynaphthaldehydebenzoylhydrazone(HNPBH)

3.1.2. Effect of Solvent

Of the various solvents [Chloroform, benzene, carbon tetrachloride, isobutanol, ethanol, dioxane and *N,N*-dimethylformamide (DMF)] were tested for the system, DMF was found to be the best solvent for the system. In 50±2% v/v DMF medium, however maximum absorbance was observed; hence a 50% DMF solution was used in the recommended procedure.

3.1.3. Effect of Acidity

Of the various acids (nitric, hydrochloric, sulfuric and phosphoric) studied, sulfuric acid was found to be the best acid for the system. The absorbance was at a maximum and constant, when the 10-mL solution (0.1 μg mL^{-1}) contained (0.3-2.5-mL) of 0.0005 mol L^{-1} H$_2$SO$_4$ at room temperature (25 ± 5°C). Outside this range of acidity the absorbance decreased. For all subsequent measurements, 1-mL of 0.0005 mol L^{-1} H$_2$SO$_4$ was added.
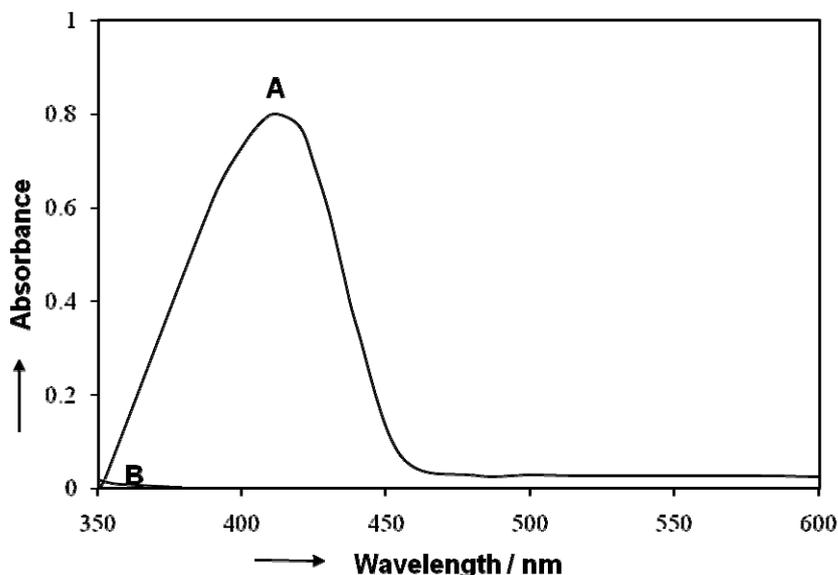
Fig.2. A and B absorbance spectra of Al^{3+} - HNPBH system and the reagent blank (λ_{max}=412nm) in aqueous solutions

3.1.4. Effect of Time

The reaction is instantaneous. The Al-HNPBH system attained maximum and constant absorbance immediately (within 1 min) after diluting the solution to the final volume, which then remained stable for at least 24 h. A longer period of time was not studied.

3.1.5. Effect of Reagent Concentration

The excess of reagent is not critical. In the test with, 1 µg mL^{-1} Al, Al/reagent mole ratio was varied from 1:10 to 1:400. Constant maximum absorbance was obtained for mole ratios between 1:70 to 1:280. For the different Al concentrations an identical effect of varying the reagent concentration was noticed. For all subsequent measurements 1-mL of 3.44×10^{-3} mol L^{-1} HNPBH solution was added.

3.1.6. Calibration Graph and Beer's Law

Plots of absorbance against Al concentration were linear and passed through the origin for a wide range (10 µg L^{-1} - 2 mg L^{-1}) of Al concentration, when different scale expansion was used. The average molar absoptivity and the Sandell's sensitivity [33] were found to be 2.21×10^4 L mol^{-1} cm^{-1} and 6 ng of Al cm^{-2} respectively. Of two calibration graphs first one pass through the origin and second one showed the deviation from linearity (Fig. 3). The selected analytical parameter obtained with the optimization experiments are summarized in Table 2.
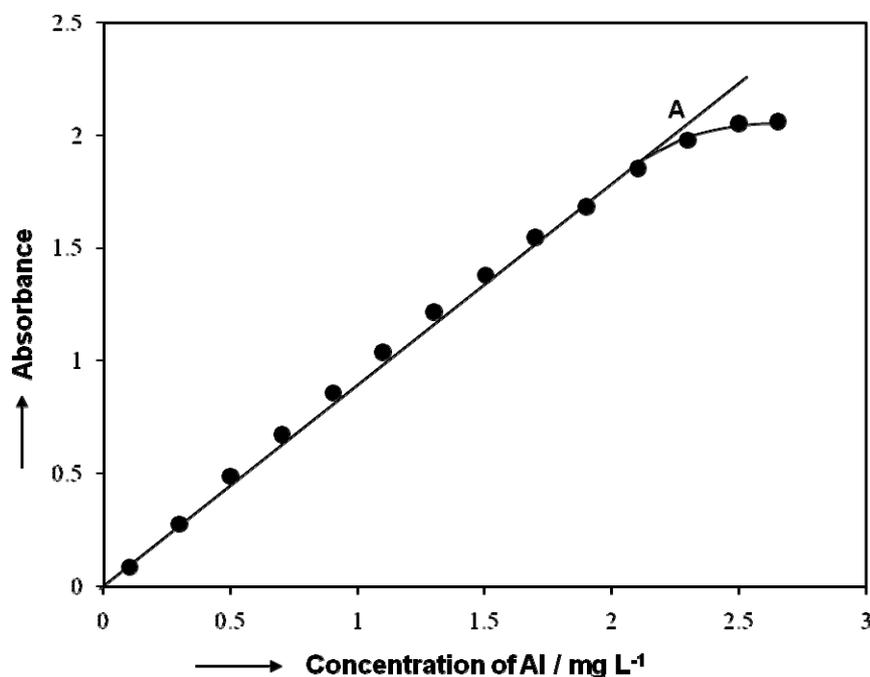
Fig.3. Calibration graph B, 0.1-2.0 mg L^{-1} od Al

3.1.7. Effect of Foreign Ions

More than 50 anions, cations and complexing agents were studied individually to investigate their effect on the determination of 0.1 µg mL^{-1} of Al. The criterion for interference was an absorbance value varying by more than 5% from the expected value for Al alone [34]. There was no interference from the following: 1000-fold amounts of nitrate, chloride, thiocyanide, azide, ammonium, alkali metals or acetate; 200-fold amounts of bromide or iodied. 100-fold amounts of arsenic(III & V) cerium(IV), magnesium, barium, sulfide, tin(II and IV), silver(I), cadmium, manganese(II), bismuth, chromium(VI), calcium, mercury(II), tungsten(VI), lead(II), 1,10-phenanthrolin, ascorbic acid, sulphate, DMG, strontium, selenium(IV and VI), arsenic(III), uranium(VI). 50-fold amount of tellurium, oxine and cyanide, molybdenum (VI), 10-fold amount of EDTA, fluoride, phosphate, tartrate. 1,10-phenanthrolin prevented the interference from a 10-fold amounts of iron(II and III), zinc, nickel(II), copper(II), cobalt(II and III). 10-fold EDTA prevented the interference from a 10-

fold amount of vanadium(V). During the interference studies, if a precipitate was formed, it was removed by centrifugation. The amount mentioned is not the tolerance limit but the actual amount studied. However, for those ions whose tolerance limit has been studied, their tolerance ratios are mentioned inTable 3. The tolerance ratio was calculated by x /Al i.e. fold amount of foreign ion / fold amount of Al.

Table 2. Selected analytical parameters obtained with the optimization experiments.

Parameters	Studied range	Selected value
Wavelength / λ_{max} (nm)	200-800	412
Acidity / mol L^{-1} H_2SO_4	1.0×10^{-5} - 2.0×10^{-4}	1.5×10^{-5} - 1.25×10^{-4} (preferably, 5×10^{-5})
pH	6.8 - 4.2	5.5 – 4.5 (preferably, 5)
Time / h	0 - 72	1 min – 24 h (preferably, 5 min)
Solvent / % DMF	20 - 70	40 – 70 (preferably, 50)
Temperature / °C	25±5	25±5
Reagent (fold molar excess, M:R)	1:10-1:450	1:70 – 1:280 (preferably, 1:90)
Average molar absorption Co-efficient / L mol^{-1} cm^{-1}	1.75×10^4-2.68×10^4	2.21×10^4
Linear range / mg L^{-1}	0.001-100	0.01 – 2.0
Detection limit / µg L^{-1}	0.05 – 10	1
Sandell's sensitiveity / ng cm^{-2}	1 - 100	6
Reproducibility (% RSD)	0 – 2	0-2
Regression co-efficient	0.9985-0.9999	0.9992

Table 3. Table of tolerance limits of foreign ions[a]

Species x	Tolerance ratio [Species (x) / Al (w/w)]	Species x	Tolerance ratio [Species (x) / Al (w/w)]
Acetate	1000	Lead (II)	100
Iron (II)	20[d,e]	Magnesium (II)	100
Ammonium (I)	1000	Manganese (II)	100
Arsenic (III)	100	Mercury (II)	100
Arsenic (V)	100	Molybdenum (VI)	20[b]
Ascorbic acid	100	Nickel (II)	10[c]
Azide	1000	Nitrate	1000
Barium	100	Phosphate	20
Beryllium(II)	100	Potassium	1000
Bromide	200	Selenium (IV)	100
Cadmium	100	Selenium (VI)	100
Calcium(II)	100	Silver	100
Cesium (II)	100	Sodium	1000
Chloride	1000	Strontium	100
Chromium (III)	100	Tartrate	10
Chromium (VI)	100	Tellurium	50
Copper (II)	10[d,f]	Thiocyanate	1000
Cyanide	50	Tin (II and IV)	100[a]
EDTA	10	Tungsten (VI)	100
Fluoride	10	Vanadium (V)	10[b]
Iodide	200	Zinc(II)	10[d]

[a]Tolerance limit was defined as ratio that causes less than 5 percent interference
[b]with 10 mg L^{-1} EDTA
[c]with 10 mg L^{-1} DMG (dimethylglyoxime)
[d]with 10 mg L^{-1} 1,10-phenantroline
[e]with 10 mg L^{-1} SCN[-]
[f]with 10 mg L^{-1} Oxine

3.1.8. Nature of Complex

Job's method[35] of continuous variation and the molar-ratio[36] method were applied to ascertain the stoichometric composition of the complex. A 2:3 (Al:HNPBH) complex was indicated by both the methods.

3.2. Analytical Applications

3.2.1. Determination of Aluminum in Synthetic Mixture

Several synthetic mixture of varying composition containing aluminum and diverse ions of known concentration were determined by present methods and the results were found to be highly reproducible. The results are shown in Table 4. Accurate recoveries were achieved in all solutions.

Table 4. Determination of aluminum in some synthetic mixtures.

Sample	Composition of mixtures (mg L^{-1})	Aluminum(III) / mg L^{-1}		
		Added	Found^a	Recovery $\pm$ s^b (%)
A	Al^{3+}	0.50	0.49	98 $\pm$ 0.5
		1.00	1.00	100 $\pm$ 0.0
B	As in A + Mg^{2+}(25) + W^{6+}(25)	0.50	0.49	98 $\pm$ 0.6
		1.00	0.99	99 $\pm$ 0.3
C	As in B + Sr^{2+}(25) + Mn^{2+}(25)	0.50	0.50	100 $\pm$ 0.0
		1.00	1.00	100 $\pm$ 0.0
D	As in C + Ba^{2+}(25) + Pb^{2+}(25)	0.50	0.52	104 $\pm$ 0.7
		1.00	1.03	103 $\pm$ 0.6
E	As in D + As^{3+}(25) + Ag^+(25)	0.50	0.53	106 $\pm$ 0.8
		1.00	1.07	107 $\pm$ 1.0
F	As in E + Cd^{2+}(25) + Ca^{2+}(25)	0.50	0.54	108 $\pm$ 1.2
		1.00	1.09	109 $\pm$ 1.5

^{a} Average of five analyses of each sample
^{b} The measure of precision is the standard deviation (SD).

3.2.2. Determination of Aluminum in Alloys and Steels

A 0.1 g amount of an alloy or steel sample containing (3.34-90.5) % Al was weighed accurately and placed in a 50-mL Erlenmeyer flask following a method recommended by Parker [37]. To this way added 5-mL each of conc. hydrochloric and nitric acid and the mixture was heated gently. 1-mL of perchloric acid (sp. Gr. 1.70) was added to the solutions and evaporated until strong fuming occurred. The solution was cooled to room temperature after complete dissolution of the sample. The soluble salts were dissolved in deionized water. The solution was filtered through a Whatman no. 40 filter paper into a 10-mL calibrated flask. The residue (silica and tungstenic acid) was washed with a small volume (5-mL) of hot (1:99) sulfuric acid by water. The filtrate and washing were collected in the some calibrated flask. The content of the flask was neutralized with dilute NH_4OH the volume was made up to the mark with deionized water.

An aliquot (1-2)-mL of this solution was pipetted into a 10-mL calibrated flask and the Al content was determined as described in general procedure using 1,10 phenanthrolin as a masking agent. Based on five replicate analysis average aluminum concentration determined by spectrophotometric method was in good agreement with the certified values. The results are shown in Table 5.

Table 5. Determination of aluminum in certified reference materials.

Certified Reference Materials (Composition, %)	Aluminum, %		
	Certified value	Found[*] (n=5)	R.S.D. %
Bureau of Analyzed Samples Ltd. No. BAS-20b (Al, 90.5 ; Mg, 1.6 ; Cu, 4.1 ; Ni, 1.9 ; Fe, 0.43 ; Mn, 0.19 ; Si, 0.24)	90.50	90.35	0.5
Bureau of Analyzed Samples Ltd. No. BAS-10g (High tensile) (Cu, 60.8; Sn, 0.21; Zn, 30; Al, 3.34; Pb, 0.023; Ni, 0.16; Fe, 1.56; Mn, 1.36)	3.34	3.30	1.2

[*]Average of five analyses of each sample

3.2.3. Determination of Aluminum in Environmental Water Sample

Each filtered (through a Whatman no. 40 filter paper) environment water sample (500-mL) evaporated nearly to dryness with a mixture of 1.5-mL HCl and 5-mL concentrated HNO_3 in a fume cupboard, following a method recommended by Greenberg *et al*[38]. and was heated with 10-mL of deionized water in order to dissolves the salts. The solution was than cooled and neutralized with dilute NH_4OH. It was transferred into 50-mL volumetric flask and diluted up to the mark with deionized water.

1 mL of the final solution was pipetted into a 10-mL calibrated flask and the Al content was determined as described in general procedure, using 1,10 phenanthrolin as a masking agent. The analysis of environmental water samples for aluminum from various sources is shown in Table 6.

3.2.4. Determination of Aluminum in Biological Samples

Human blood (2-5-mL) and urine (20-30-mL) was collected in polyethane bottles from the affected persons. Immediately after collection, they were stored in a salt-ice mixture and later, at the laboratory, were kept at -20°C. The samples were taken into a 100-mL micro-Kjeldahl flask. Glass bead and 10-mL of concentrated nitric acid were added and the flask was placed on the digester under gentle heating. When the initial brisk reaction was over, the solution was removed and cooled following a method recommended by Stahr[39]. 1-mL volume of concentrated sulfuric acid was added carefully, followed by the addition of 2-mL of concentrated HF, and heating was continued for at least ½ hr and then cooled. The solution of flask then neutralized with dilute NH_4OH solution. The resultant solution was then transferred quantitatively into a 10-mL calibrated flask and made up to the mark with deionized water.

A suitable aliquot (1-2-mL) of the final solution was pipetted into a 10-mL calibrated flask and the aluminum content was determined as described under the procedure using 1,10 phenanthrolin as masking agent. The results of biological analyses by the spectrophotometric method were found to be in excellent agreement with those obtained by AAS. The results are shown in Table 7

3.2.5. Determination of Aluminum in Soil Samples

A 100 g amount of air-dried soil sample was weighed accurately and placed in a 100-mL micro-kjeldahl flask. The sample was digested according to the method recommended by Jackson [40]. The contents of the flask were filtered through a Whatman no. 40 filter paper

into 25-mL calibrated flask neutralized with dilute NH_4OH and diluted to the volume with deionized water.

Suitable aliquots (1-2-mL) were transferred to a 10-mL volumetric flask and the calculated amount of 0.0005 M H_2SO_4 needed to give a final acidity, followed by 1-mL of 1,10 phenanthrolin (0.1%) solution. Al content was then determined as in general procedure. The results are shown in Table 8.

Table 6. Determination of aluminum in some environmental water samples.

Sample		Aluminium / $\mu g\ L^{-1}$		Recovery ± s (%)	$s_r^{\ b}$ (%)
		Added	Found [a]		
Tap water		0	52.0		
		100	150.0	98.7 ± 0.5	0.25
		500	555.0	100.5 ± 0.6	0.28
Well water		0	31.0		
		100	130.0	100.8 ± 0.6	0.13
		500	532.0	100.2 ± 0.4	0.15
River water	Karnaphuly (upper)	0	23.0		
		100	120.0	97.6 ± 1.0	0.16
		500	525.0	100.4 ± 1.2	0.12
	Karnaphuly (lower)	0	21.0		
		100	120.0	99 ± 0.5	0.18
		500	525.0	99 ± 0.6	0.24
	Halda (upper)	0	16.0		
		100	118.0	101.7 ± 1.0	0.45
		500	520.0	100.8 ± 0.8	0.38
	Halda (lower)	0	15.0		
		100	116.0	99 ± 0.3	0.15
		500	515.0	100 ± 0.0	0.00
Sea water	Bay of Bengal (upper)	0	13.0		
		100	115.0	101.7 ± 1.3	0.18
		500	520.0	101.4 ± 1.5	0.26
	Bay of Bengal (lower)	0	12.0		
		100	113.0	100.8 ± 0.8	0.39
		500	515.0	100.5 ± 1.0	0.49
Drain water	KPM[c]	0	45.0		
		100	146.0	100.9 ± 0.8	0.33
		500	550.0	100.9 ± 0.6	0.46
	KAPCO[d]	0	30.0		
		100	132.0	101.5 ± 1.5	0.44
		500	535.0	100.9 ± 1.8	0.42
	Aluminium Factory[e]	0	55.0		0.52
		100	156.0	100.6 ± 1.6	
		500	560.0	101.8 ± 1.8	0.56
	Modina Tanery[f]	0	42.0		
		100	140.0	98.6 ± 1.2	0.34
		500	545.0	100.5 ± 1.5	0.38

[a] Values of given represent the average of five analyses of each sample.
[b] Relative standard deviation is a measure of precision (s_r)
[c] Karnafuly Paper Mill, Chandraghona, Chittagong
[d] Karnafuly Fertilizer Company, Rangadia, Chittagong
[e] Aluminium Factory, Near Sugandha R/A, Chittagong
[f] Madina Tanery, Jalalabad, Chittagong

Table 7 Concentration of aluminum in human blood, urine and gallstone samples.

| Serial No. | Sample source[a] | Sample | Aluminum / $\mu g\ L^{-1}$ | | | |
| | | | AAS (n = 5) | | Proposed method (n = 5) | |
			Found	RSD, %	Found	RSD, %
1	Normal adult	Blood	130.0	1.0	132.59	1.2
	(Male)	Urine	42.5	1.6	45.0	1.5
2	Cancer patient	Blood	312.0	1.5	315.0	1.2
	(Leukemia)	Urine	128.0	1.8	131.0	1.6
3	Lung cancer (Male)	Blood	271.0	1.8	275.0	1.5
		Urine	90.5	2.0	95.5	1.8
4	Gallstone patient	Human	29.0[b]	1.5	45.5[b]	1.2
	(Male)	gallstone				

[a]Samples were collected from Chittagong Medical College Hospital, Chittagong.
[b]Values in mg kg^{-1}.

Table 8 Determination of aluminum in some surface soil.

Serial No.	Sample source	Aluminum (mg kg^{-1})[a]
S_1[c]	Marine soil	4.5 ± 1.5[b]
	(Bay of Bengal, Potenga, Chittagong)	
S_2	Estuarine soil	7.4 ± 1.2
	(Junction of Bay of Bengal and Karnaphuly River, Chittagong)	
S_3	Road side soil	8.4 ± 1.0
	(Fatehabad, Hathazari, Chittagong)	
S_4	Agriculture soil	8.6 ± 0.8
	(From Jobrha Village, Near University of Chittagong)	
S_5	Industrial soil	13.6 ± 0.5
	(Modina Tanery, Jalalabad, Chittagong)	

[a]Average of five analyses of each sample
[b]Measure of precision is the standard deviation(s)
[c]Composition of the soil samples: C, N, P, K, Al, Na, Ca, Mg, Cu, Fe, Pb, NO_3, NO_2, Zn, SO_4, Mn, Mo, Co, etc.

3.2.6. Determination of Aluminum in Pharmaceutical Samples

Finished pharmaceutical sample (Al containing tablets) were quantitatively taken in a beaker. Add 10-mL of concentrated nitric acid and heated to dryness and than added 10-mL of 20% (v/v) of HCl and 1-2 drops $HClO_4$. The volume was reduced to 2-5-mL and then cooled to room temperature. The solution was than neutralized with dilute NH_4OH. The resulting solution was then filtrated and quantitatively transferred to a 25-mL calibrated flask and made upto the mark with distilled water, and aluminum content was measured by general procedure using 1,10-phenanlhrolin as a masking agent and the result is given in the Table 9. The results of some pharmaceutical tablets are in good agreement with the reported values.

Table 9. Determination of aluminum in some pharmaceutical samples.

| Serial No. | Sample source | Composition of tablet | Trade name | Aluminum / mg g^{-1} | | RSD % |
				Reported	Found	
1	Square Pharmaceutical	400 mg	Entacyd	98.1	99.8	1.5
2	United Pharmaceutical	300 mg	Almasil MS	146.5	143.5	2.0

3.2.7. Precision and Accuracy

The precision of the present method was evaluated by determining different concentrations of Al (each analyzed at least five times). The relative standard deviations (n = 5) in the range 2-0 for 0.1-20 µg of Al in 10-mL were achieved, indicating that this method is highly precise and reproducible. The detection limit (3s of the blank) for Al was found to be $1 \mu g L^{-1}$. The reliability of the proposed procedure was assessed by analyzing the certified reference materials (Table 5) and a series of synthetic mixtures of various compositions (Table 4). Note from Table 5 the good agreement for Al found with the certified values. A few synthetic mixtures of various composition containing Al and diverse ions of known concentrations were determined by the present method using 1,10-phenanthrolin as masking agents, and the results (Table 4) were found to be highly reproducible. The reliability of our procedure was also tested by doing recovery studies. The average recovery obtained for the addition of Al spikes to some environmental water samples was quantitative, as shown in Table 6. The results of the analysis of biological samples by our procedure were found to be in excellent agreement with those obtained by an atomic absorption spectrophotometric method, as shown in Table 7. Hence, the precision and accuracy of the method were found to be excellent.

4. Discussion on Applications

The proposed method was used to determine the Al content of a series of synthetic mixtures of various compositions. The method was also applied to the determination of the Al content in a number of standard samples (alloys and steels), environmental water (inland and surface), biological samples (human gallstone, blood and urine), soil and pharmaceutical samples. In view of the unknown composition of the environmental water samples, the same aliquots were analyzed for their Al content, both "spiked" and "un-spiked". The mean error and standard deviation for each series of determination were calculated.

A few synthetic mixture of varying composition containing Al and diverse ions of known concentrations were determined by the present method and the corresponding results are given in (Table 4).The reliability of the proposed method was assessed by analyzing the certified reference materials and corresponding results are shown in (Table 5).The analysis of water from various sources for Al is shown in (Table 6). The high values for treated waters are probably due to leakage or excess addition of alum used as a flocculants in the water-treatment plants. The occurrence of such high values of Al content are also reported in the treated waters of some developed countries [41]. The results of the analysis of biological samples by proposed procedure were found to be in excellent agreement with those obtained by atomic absorption spectrophotometric methods and are shown in (Table 7). The abnormally high value for the cancer (Leukemia) patient is probably due to the involvement of a high aluminum concentration with As and Zn. The occurrence of such high aluminum contents has also been reported in cancer patient from some developed countries [3]. The average value of Al in five different surface soil samples of Bangladesh was found to be 8.5 mg kg^{-1}. The results are show in (Table 8). The method is very reliable, and the concentration in the ng g^{-1} range in aqueous solutions at room temperature (25±5˚C) can be measured in a very simple and rapid way for routine analysis of Al.

5. Conclusions

In this paper, a new, simple, sensitive, selective and less expensive method with Al(III)-HNPBH complex was developed for the determination of aluminum in some real, biological, soil, environmental water and pharmaceutical samples for continuous monitoring to establish the trace levels of aluminum in different sample matrices. Although many

sophisticated techniques such as pulse polarography, HPLC, AAS, ICP-AES, ICP-MS, etc. are available for the determination of aluminum at trace levels in numerous complex materials, factors such as the low cost of the instrument, easy handling, lack of requirement for consumables and almost no maintenance have caused spectrophtometry to remain a popular technique, particularly in laboratories of developing countries with limited budget. The sensitivity in terms of molar absorptivity and precision in terms of relative standard deviation of the present method are very reliable for the determination of aluminum in real samples down to ng g^{-1} levels in aqueous medium at room temperature (25 ± 5°C).

References

1. Browar H, Importance of aluminum http:// www.firstaluminum.com/articles.

2. Li Z, Lu N, Zhou X and Song Q (2007) Extraction spectrophotometric determination of aluminum in dialysis concentrates with 3,5-ditertbutylsalicyl -fluorone and ionic liquid 1-butyl-3-trimethylsilylimidazolium hexafluorophosphate. J Pharma 43(5) : 1609

3. Venugopal B and Luckey T D (1979) Aluminum in, Metal Toxicity in Mammals 2, Plenum, New York, p 104

4. Abubakar MG, Taylor A and Ferns GA (2004) The effect of Aluminum and Selenium supplementation on brain and liver antioxidant status in rat. Afr J Biotechnol 3(1): 88.

5. Hassan NI and Ahmad M (2007) Analysis Kvantitatif aluminum(III) menggunakan reagent Alizarin Red S dan Jaringan neural tiruan(ANN). Sins Malaysian 36(2) : 189.

6. Kamino S, Yamaguchi T, Mori T, Miyamoto M, Kusumi Y and Fujita Y (2005) Spectrophotometric Determination of Aluminum with *m*-Carboxyphenylfluorone, a Novel Chemical Probe and Its Application. Anal Sci 21(12) :1549

7. Zhou N (2004) Selective Spectrophotometric Determination of Aluminium in the Presence of Beryllium and Lanthanide Cations. Microchimica Acta 146(1) : 73.

8. Idriss KA, Hashem EY, Aziz MSA and Ahmed HM (2000) Direct spectrophotometric determination of aluminum oxide in Portland cement and cement clinker. An insight into the solution equilibria and analytical aspects of the aluminum–quinizarin system. Analyst 125: 221.

9. Zareba S and Melke J (2000) Spectrophotometric determination of aluminum in pharmaceutical preparations by azo dyes of 1,2,4-triazole series. Pharm Acta Helv 74(4): 361.

10. Tufan G, Dilek UU, Tevfik G and Ali H (2005) 2,2′,3,4-Tetrahydroxy-3′-sulpho-5′-nitroazobenzene for spectrophotometric determination of aluminum in pharmaceutical suspensions and granite. Anal Chimica Acta 545(1) : 107.

11. Spinola A (1998) Spectrophotometric determination of aluminum in iron ores using solid-phase extraction. J Braz Chem Soc 9(2) : 151

12. Bahrama M, Madrakianb T, Bozorgzadehb T and A Afkhamib (2007) Micelle-mediated extraction for simultaneous spectrophotometric determination of aluminum and beryllium using mean centering of ratio spectra. Talanta 72(2) : 408

13. Shokrollahi M Ghaedi, Niband MS and Rajabi HR (2008) Selective and sensitive spectrophotometric method for determination of sub-micro-molar amounts of aluminum ion. J Haza Mate 151(2-3): 642

14. Niazi A, Zolgharnein J and Davoodabadi MR (2007) Simultaneous determination of aluminum and iron with hematoxylin using spectrophotometric and orthogonal signal correction-partial least squares in plant and water. Ann Chim 97(11-12): 1181

15. Zheng HL, Xiong MG, Gong YK, Peng DJ and Li LC (2007) Catalytic spectrophotometric determination of trace aluminum with indigo carmine. Spectrochim Acta A Mol Biomol Spectrosc 66(4-5): 1243.

16. Carpani I, Scavetta E and Tonelli D (2004) Spectrophotometric determination of aluminum and nickel. Ann Chim 94(5-6): 365

17. He R and Wang J (2000) Novel catalytic spectrophotometric procedure for the determination of trace-level aluminum. Anal Chemica Acta 412(1-2): 241

18. Pourreza N and Behpour M (1999) Column preconcentration of aluminum using Eriochrome Cyanine R and methyltrioctylammonium chloride adsorbent supported on naphthalene with subsequent spectrophotometric determination. Microchemical J 63(2): 250

19. Afkhami A and Zarei A R (2004) Simultaneous kinetic determination of beryllium and aluminum by spectrophotometric H-point standard addition method. Anal Sci 20(12): 1711.

20. Rizk M, Zakhari NR, Toubar SS and El-Shabrawy Y (1995) Spectrophotometric determination of aluminum and copper ions using spadns. Microchimica Acta 118(3-4): 239.

21. Buratti M, Valla C, Pellegrino O, Rubino FM and Colombi A (2006) Aluminum determination in biological fluids and dialysis concentration via chelation with 8-hydroxy quinolin and solvent extraction fluorimetry. Anal Biochem 353(1): 63.

22. Ahmed MJ and Hossan J (1995) Spectrophotometric determination of aluminum by morin. Talanta 42: 1135

23. Diaz AM, Mariscal JMH, Reguera MIP and Vallvey LFC (1993) Determination of trace of aluminum with chrome azrurol S by solid-phase spectrophotometry. Talanta 40(7): 1059.

24. Agnihotri NK, Singh HB, Sharma RL and Singh VK (1993) Simultaneous determination of beryllium and aluminum in mixtures using derivative spectrophotometry. Talanta 40(3): 415.

25. Ying-ping H, Ke-mei Y and Hua-shan Z (1999) Spectrophotometric determination of aluminum with 2,3,7-trihydroxy-9-[4-(2,4-dihydroxy)phenylazo] phenylfluorone. Wuhan University J Natural Sci 4(2) : 219.

26. Mendez JH, Martinez RC, Cordero B M and Davila LG (1983) Spectrophotometric determination of aluminium with alizarin red S sensitized with polyvinylpyrrolidone. Analytica Chimica Acta 149: 379.

27. Luo M and Bi S (2003) Solid phase extraction spectrophotometric determination of dissolved aluminum in soil extracts and ground waters. J Inorg Biochem 97(1): 173.

28. Valencia MC, Boudra S and Bosque-Sendra JM (1996) Simultaneous determination of aluminum and beryllium at the subnanogram per millilitre level by solid-phase derivative spectrophotometry. Anal Chimica Acta 327(1) : 73.

29. Azhari SJ and Amin SA (2007) Highly sensitive and highly selective spectrophotometric determination of aluminum after collection on a membrane filter using 2,3-dichloro-6-(3-carboxy-2-hydroxy-1-naphthylazo) quinoxaline and zephiramine. Anal Letters 40(15) : 2959.

30. Ahmed MJ and Nasiruddin M (2007) A simple spectrophotometric method for the determination of cobalt in industrial, environmental, biological and Soil samples using bis(salicylaldehyde)orthophenylenediamine. Chemosphere 67 (10): 2020.

31. Sacconi L (1953) Acylhydrazones of o-Oxy- and o-Aminoaldehydes and ketones as tridentate complexing agents. J Am Chem Soc 75 : 5434.

32. Salam MA, Chowdhury DA and Hossain SMA (1995) Preparation and characterisaton of Shiff base reagent. Bull Pure and Appl Sci 14C : 129.

33. Sandell EB (1965) Colorimetric determination of traces of metals, 3rd end. Interscience, New York, p 269.

34. Bosch Ojeda C, Gaecia De Torres A, Sanchez FR and Cano Pavon JM (1987) Fluorometric determination of trace amount of gallium in biological tissues. The Analyst 112: 1499.

35. Job P (1928) Stability constant of coordination compounds. Anal Chim (Paris) 9: 113.

36. Yoe JA and Jones AL (1944) Stability constant of coordination compound, Ind. Eng. Chem. Anal., Ed. 16 : 11.

37. Parker GA (1983) Analytical Chemistry of Molybdenum, Springer Verlag Berlin.

38. Greenberg AE, Clesceri LS and Trussell RR (eds) (1992) Standard Methods for the Examination of Water and Waste Water, 18th ed., American Public Health Association, Washington DC. P 3.

39. Stahr HM (1991) Analytical Methods in Toxicology, 3rd ed., John Wiley and Sons, New York p 75.

40. Jackson ML (1965) Soil Chemical Analysis, Prentic-Hall, New Jersey, p 297.

41. Uehara N, Kanbayashi M, Hosino H and Yotsuyanagi T (1989) An ion-pair reversed phase HPLC-fluorimetric system for ultra-trace determination of aluminum with salicylaldehydebenzoyalhydrazone. Talanta 36: 1031.