

Spectrophotometric Determination of Aluminum using Aurin tricarboxylic acid triammonium salt (aluminon) in the presence of Cetylpyridinium chloride as surfactant

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A facile, rapid and very sensitive method has been developed for the spectrophotometric determination of aluminum based on complexation reaction between the metal ion and aluminon in the presence of cationic surfactant cetylpyridinium chloride (CPC). The important parameters affecting the analytical procedure were optimized. Absorption maximum for a ternary complex was noted at 535 nm. The reaction was found to be rapid at room temperature and absorbance remained constant for more than one week. The method adheres to Beer's law in a range of 0.01-0.4 $\mu\text{g mL}^{-1}$ with apparent molar absorptivity of $8.24 \times 10^4 \text{L mol cm}^{-1}$ and Sandell's sensitivity 0.3 ng mL^{-1} . The effect of foreign ions was tested by taking a constant concentration of metal ion and determining its concentration in the presence of ≥ 100 folds in excess of foreign ions. The method has been applied for the determination of aluminum in the pharmaceutical formulations as well as in water samples and a good agreement was found with the values obtained by using FAAS technique. The relative standard deviation was found to be less than 3.5%.

Keywords: Spectrophotometric Determination, Aluminum, Aluminon, Surfactant CPC, Pharmaceutical Products, Water samples

1. Introduction

Aluminum is among the third most abundant metals in the earth's crust, with a mean concentration of 8.13 % by weight[1]. Familiar uses of aluminum are in beverage cans, pots and pans, airplanes, and foil. Aluminum compounds are used in different products such as antacids, astringents, buffered aspirin, food additives, and antiperspirants. In most of the natural waters, the concentration of aluminum is reported to be low due to limited solubility at the pHs normally encountered in fresh water. As a result of human activities, a considerable mobilization of aluminum has occurred. It is very difficult to elucidate the complete distribution of aluminum compounds in natural waters because of the large number of compounds, that all participate in dynamic interaction; the total concentration of aluminum, ranging from a few $\mu\text{g L}^{-1}$ in transparent neutral waters to mg L^{-1} in brownish water of low pH and the presence of organic and other substances that might interfere with its determination[2,3].

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Among bio applications, aluminum is considered as an essential element in the nutrition of animals and humans as it acts as cofactor in numerous enzymes and play an important role in protein synthesis and cell division [4]. It also plays important role in the maintenance of cell membrane stability and in the function of immune system. It also constitutes an active ingredient in medical products intended for tropical applications. Aluminum deficiency may effect severely therefore, it is important to monitor its concentration in both environmental water samples and pharmaceutical formulations.

The organic reagents for the spectrophotometric determination of aluminum include pyrocatechol violet, Ferron, Oxine(8-Hydroxyquinoline), Eriochrome cyanine R and chromazurol S. Among many spectrophotometric determination methods of aluminum chromeazurol-S, pyrocatechol-violet, 8-hydroxyquinoline, ferron and eriochrome cyanine-S were commonly used [5-10]. However, most of these methods were reported less sensitive. Various other reports have indicated some new hydrazones, semicarbazones and their applications to the spectrophotometric determination of aluminum were published [11-14]. The organic reagent 8-hydroxyquinoline is practically insoluble in water and combines with aluminum ions to yield a non-polar coloured complex, generally extracted into organic solvent such as chloroform and carbon tetrachloride. These are time consuming, tedious and involve the use of chlorinated solvents that cause contamination in the atmosphere. They offer however, no significant progress with respect to either sensitivity or selectivity in comparison with the method reported herein. Aluminon is a triammonium salt of 5-[(3-carboxy-4-hydroxyphenyl)(3-carboxy-4-oxocyclohexa-2,5-dien-1-ylidene)methyl]-2-hydroxybenzoic acid and it forms a water-soluble complex with aluminum which absorbs light in the visible range of 515-530 nm. It has been extensively used as a classical organic reagent for the spectrophotometric determination of aluminum in different matrices [15-20]. The complexing properties of aluminon have been used for the spectrophotometric determination of aluminum ions. However, a little attention has been directed to the spectrophotometric determination of Aluminum in micellar medium.

In the recent years, surfactants have become of great interest because of providing a reaction medium in which the sensitivity and selectivity of numerous reactions were improved [21-27]. The presence of surfactants especially cationic surfactants such as cetyltrimethylammonium chloride (CTAC), cetylpyridiniumchloride (CPC), zephiramine (Zp) have been studied for the colour reaction between various dyes and metal ions. Usually, the metal chelate complexes formed in the micellar systems are more stable than those formed in the absence of surfactants. The most remarkable advantage of surfactants includes: a) formation of the ternary complexes with the higher molar absorption i.e. increasing sensitivity, b) expansion of color reaction area or determination range, c) large bathochromic shift i.e. sharp contrast, d) resistance to the interfering ions or increase in selectivity and stability of complexes, etc. These effects show the advantage of such surfactant systems in the development of new spectrophotometric methods for determining micro amount of metals ions, anions, biological compounds, drugs and pesticides.

In present communication, a spectrophotometric method is reported that can be used for the quantitative determination of aluminum directly based on the complexation reaction between aluminum ion and aluminon in the presence of cationic surfactant CPC. Different factors affecting the reaction of aluminum in micellar media were optimized. The proposed method has been successfully applied to the determination of aluminum in water samples from different origin and pharmaceutical products. The results were compared with those obtained by employing FAAS technique and a good agreement is observed.

2. Experimental

2.1. Apparatus

A UV-visible spectrophotometer Model UV-1601 of Shimadzu (Japan) with a fixed slit width of 0.5nm and x-y recorder was used. An Orion research model 601A, digital ion analyzer fitted with a combined glass electrode was used for the adjustment and preparation of pH buffer solutions.

2.2. Reagents and solutions

Unless otherwise stated, all reagents used were of analytical grade, without further purification, and all solutions were prepared in double distilled water and ethanol as per requirement. Aluminum standard solution ($1.0 \times 10^3 \mu\text{g mL}^{-1}$) was prepared by dissolving 0.4941g of AlCl_3 (Aldrich) in distilled water and diluted to 100 ml with distilled water. Working solutions were obtained by appropriate dilution of the standard solution. Standard solution of aluminon (0.02 mol L^{-1}) was prepared by dissolving 0.9468g of reagent in ethanol and diluted the solution up to 100 ml with distilled water. Buffer solutions were prepared by mixing 0.1 mol L^{-1} solutions of hydrochloric acid and potassium chloride for pH 1-2.5, acetic acid and sodium acetate for pH 3-6, potassium dihydrogen phosphate and disodium hydrogen phosphate for pH 6-9.

Various surfactants namely, cetylpyridinium chloride (CPC), cetyltrimethyl ammonium bromide(CTAB), sodium dodecylsulfate (SDS), dioctyl sulfosuccinate sodium salt (SDSS), dodecyl benzene sulfonic acid sodium salt (SDBS), cetylpyridinium bromide (CPB), BDTA, Triton X-100 and Tween-20 were procured from E. Merck (F. R. Germany) and their 0.01 mol L^{-1} solutions were prepared in water,

2.3. Determination of Al^{3+} in water samples

Different water samples such as Tape and River water (1 L) were collected from River Jehlum and River Neelum in and around the city of Muzaffarabad. The samples were stored at $\leq 5^\circ\text{C}$ in metal free polyethylene bottles. The water samples were filtered through a Whatman filter paper No 41 in a Pyrex glass beakers. The contents were evaporated to nearly dryness and re-dissolved with 10 ml of double distilled water. Then the solution was transferred into a 25 ml measuring flask and made up to the volume with double distilled de-ionized water.

2.4. Determination of Al^{3+} in Pharmaceutical formulations

Three commercial pharmaceutical samples ALUMICO (Aluminum hydroxide plus magnesium hydroxide suspension; Regent Laboratories, Karachi, Pakistan), ACTAL (Pharmatec, Pakistan) and GASNIL (Davis pharmaceutical laboratories, Pakistan) tablets were used for determination of aluminum contents. The pretreatment to these samples are as follows:

A 5.0 ml portion of ALUMICO suspension was evaporated to dryness and the soluble salts were dissolved with 2.0 ml concentrated sulfuric acid and added 10 mL de-ionized water. The solution was filtered to remove the insoluble

residue and washed three times with water. The filtrate was made up to 25 ml in a measuring flask and used as a working solution for aluminum determination. One tablet of each ACTAL and GASNIL was ground in a mortar with piston separately and a known weight of (50mg) each ground sample was treated with 3.0 ml of concentrated sulfuric acid. The solution was heated to near dryness then 10 mL of deionized water was added and filtered to remove the white residue. The filtrate and the washing were kept in a 50 ml volumetric flask and made the volume with distilled water. The resulting solution was used as a working solution for aluminum determination.

3. General Determination Procedure

A sample solution containing 4.5 μg of Al^{3+} was transferred to a 25 ml measuring flask then 1.0 ml of (0.02 mol L^{-1}) aluminon was added to it and mixed well. The pH was adjusted by adding 5.0 ml of the acetate buffer solution of pH 5.0 to the above mixture followed by the addition of 2.0 ml of 0.01 mol L^{-1} CPC solution and diluted to the mark with distilled water. The solution was mixed well and the absorbance was measured at 535 nm in 1 cm cuvette, against a reagent blank prepared in the same manner without metal ions.

4. Results and discussion

4.1. Selection of Suitable Surfactant

For the selection of proper surfactant, nine different surfactants namely, CPC, CTAB, SDS, SDSS, SDBS, CPB, BDTA, Triton X-100 and Tween-20 were tested. The effect of 1.0 ml of 0.01 mol L^{-1} of each surfactant on the absorbance using fixed amount of aluminum (4.5 $\mu\text{g}/25\text{mL}$), pH 5.0 and 535 nm (λ_{max}) was determined (Figure 1). The figure shows a maximum enhancement in the absorbance while using CPC. Therefore, for further study, CPC was selected as the most suitable surfactant and it was used for optimization of all other experimental parameters.

The absorption spectra of aluminon, Al-aluminon and Al-aluminon-CPC using 0.5 mL (0.02 mol L^{-1}) of aluminon, 9.0 μg of aluminum and 1.0 mL of CPC (0.01 mol L^{-1}) for a 25 mL final volume (made with pH 5.0 buffer solution) were recorded and shown in Figure 2. The results showed a maximum absorbance at 525 nm and 535 nm for Al-aluminon and Al-aluminon-CPC complexes, respectively. Although a small change i.e. 10 nm in the λ_{max} was observed but appreciable enhancement in the absorption by the use of CPC was recorded. Therefore, 535 nm was selected as λ_{max} for further studies.

4.2. Conditions of complex formation

The influence of pH on the absorbance of ternary Al-aluminon-CPC complex was studied over the pH range of 4.0-6.5 and maximum absorption was obtained at pH 5.0 (Figure 3). The effect of the volume of buffer solution (pH 5) on the absorbance is shown in Figure 4, showing that 5 mL of pH 5.0 buffer solution is sufficient for the maintenance of pH of the final volume.

The effect of varying concentration of the aluminon from 0.1 - 3.0 mL of stock solution (0.02 mol L^{-1}) on the color development using 4.5 μg Al^{3+} and 1.0 ml of 1.0×10^{-2} mol L^{-1} surfactant per 25 ml final volume was examined by measuring the absorbance. A complete colour development was obtained in the presence of 1.0 ml of 2.0×10^{-2} mol L^{-1} aluminon as shown in Figure 5. The effect of the concentration of CPC on the formation of ternary complex was studied over the range of 0.1 - 2.5 mL of 0.01 mol L^{-1} of stock solution. It was found that 2.0 mL of CPC solution of 1.0×10^{-2} mol L^{-1} concentration is sufficient for maximum enhancement in the absorbance (Figure 6).

It was further noted that complex formation reaction is independent of the order of addition of different reactants. However, Al^{3+} solution was followed by the addition of reagent solution then buffer solution and lastly CPC was added in the proposed method. The reaction is spontaneous at room temperature and colour development of ternary complex is completed immediately after the addition of the reagents; however, the absorbance was taken after 10 min. The absorbance was found to be stable for one week and no detectable change was observed in colour intensity with rising in temperature up to 45 $^{\circ}\text{C}$.

The calibration graph between the metal ions and absorbance was constructed following the general procedure in the absence as well as in the presence of CPC and the results are presented in Figure 7. The calibration curve followed the Beer's law up to 0.3 $\mu\text{g mL}^{-1}$ and 0.4 $\mu\text{g mL}^{-1}$ in the absence and in the presence of CPC, respectively. The linear regression equations of $Y = 1.2837X$ with correlation coefficient 0.997 in the absence of CPC and $y = 3.0558X$ with correlation coefficient 0.9997 in the presence of CPC were obtained showing 2.4 fold enhancement in the sensitivity of the proposed method. Molar absorptivity and Sandell's sensitivity of the proposed method was estimated

to be $8.244 \times 10^4 \text{ L mol cm}^{-1}$ and $0.3 \mu\text{g mL}^{-1}$, respectively. The main conditions and characteristics of the proposed method are summarized in Table 1. The relative standard deviations at a concentration level of $0.20 \mu\text{g mL}^{-1}$ of aluminum (five replicate determinations) were calculated and found to be 0.21 ± 0.0066 showing a good accuracy and precision of the proposed method.

4.3. Effect of foreign ions

The selectivity of the proposed spectrophotometric method was investigated by determining the absorbance of $0.18 \mu\text{g mL}^{-1}$ aluminum in the presence of various foreign ions. Sodium or potassium salts were used for anionic study whereas, chloride and nitrate salts were used for cations concentrations greater than 100-fold excess over the aluminum concentration and the results are presented in Table 2. It was found that only Fe^{3+} and Ag^{+1} interfere in determination of aluminum. All the other anions and cations studied have no appreciable effect on determination of aluminum.

5. Analytical application

The method was applied for the determination of Al^{3+} ions in tap water and river water and no detectable aluminum was found. To determine the accuracy of the method, a known amount of aluminum was determined. Two ml of pre-concentrated water sample was taken into a 10 ml measuring flask and spiked with known amount of aluminum and contents were determined following the general determination procedure. Absorbance was measured after 10 minutes at 535 nm, relative to a blank prepared in the same way except the addition of aluminum (Table.3). The results shows a good recovery of aluminum from water samples.

5.1. Pharmaceutical formulations

A known volume of working solution of pharmaceutical samples was taken in a 25 ml flask and aluminum contents were determined by employing the spectrophotometric method developed herein. The amount of aluminum was also determined by flame atomic absorption spectrometry and the results were compared (Table-3). The results obtained by both the techniques agreed well with each other showing a good accuracy and selectivity of the reported method for the determination of aluminum in pharmaceutical samples using aluminum and CPC.

6. Conclusions

The proposed spectrophotometric method for the determination of aluminum in the presence of CPC is selective, rapid and simple. Application of surface-active substances play a better role in the Al^{3+} -aluminon complex formation and creates better condition to enhance the sensitivity of the method. The proposed method can be employed directly for the measurement of the absorbance of analyte containing aluminum ions without heating or waiting. The Beer's law is obeyed over the Al^{3+} concentration range $0.01\text{-}0.4 \mu\text{g mL}^{-1}$. Many existing parameters such as Molar extension coefficient, stability of the complex and Sendell's sensitivity have been improved. The proposed methods is precise, highly selective, sensitive and equally applicable for the determination of aluminum in aqueous solution, environmental water samples and pharmaceutical products.

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Captions

Figure 1. Effect of various surfactants on the Al-Aluminon complex.

Figure 2. Absorption spectra of the Aluminon (curve 1), and Al-aluminon complex containing 1mL of CPC (0.01 mol L^{-1}) in acetate buffer of pH 5.0 for 25 ml final solution.

$\text{Al}^{3+} = 9.0 \text{ } \mu\text{g}$; Aluminon = 0.5 mL of 0.01 mol L^{-1}
buffer solution = 5.0 mL

Figure 3. Effect of pH on Al-aluminon-CPC-system

Figure 4. Effect of various volume (in mL) of acetate buffer solution of pH 5.0 on the absorbance

Figure 5. Absorbance as a function of aluminon concentration (mL of 0.02 mol L^{-1})

Figure 6. Effects of various volume of $1.0 \times 10^{-2} \text{ M}$ CPC on the absorbance of Al-aluminon-CPC complex.

Figure 7. Calibration curves of Al-aluminon and Al-aluminon-CPC complexes

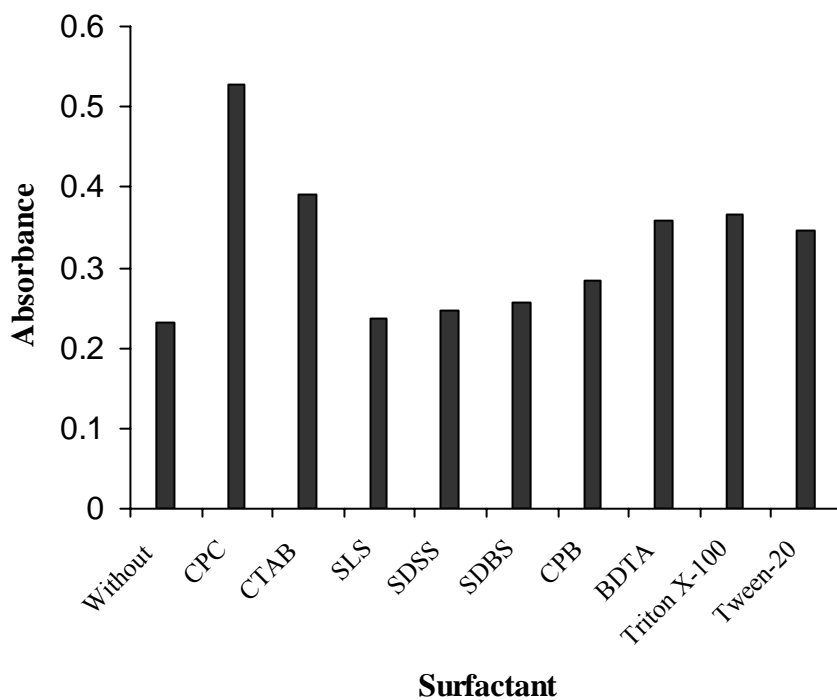


Figure 1. Effect of various surfactants on the Al^{3+} -Aluminon complex.

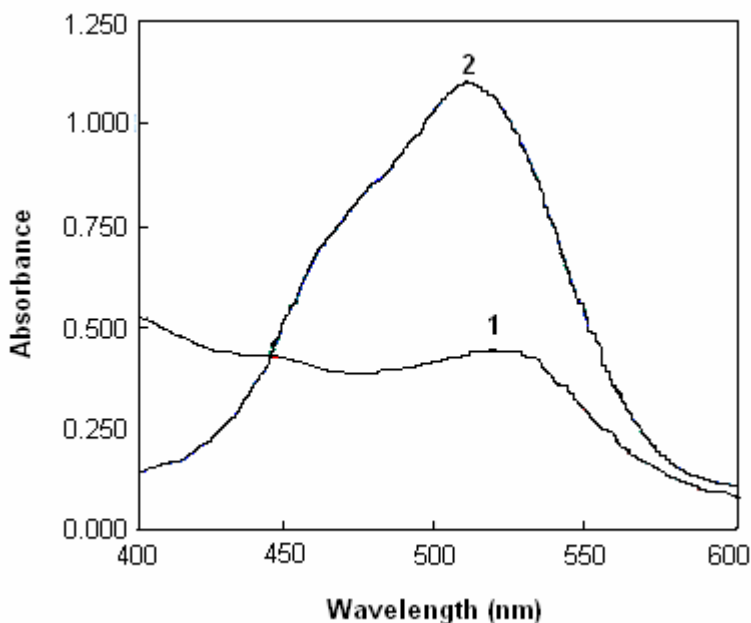


Figure 2. Absorption spectra of the Aluminon (curve A), aluminon- CPC (curve B), and Al^{3+} -aluminon-CPC complex (curve C) in acetate buffer of pH 5.0 for 25 ml final solution.

$\text{Al}^{3+} = 9.0 \mu\text{g}$; Aluminon = 0.5 mL of 0.01 mol L^{-1}
 CPC = 1.0 mL of 0.01 mol L^{-1} ; buffer solution = 5.0 mL

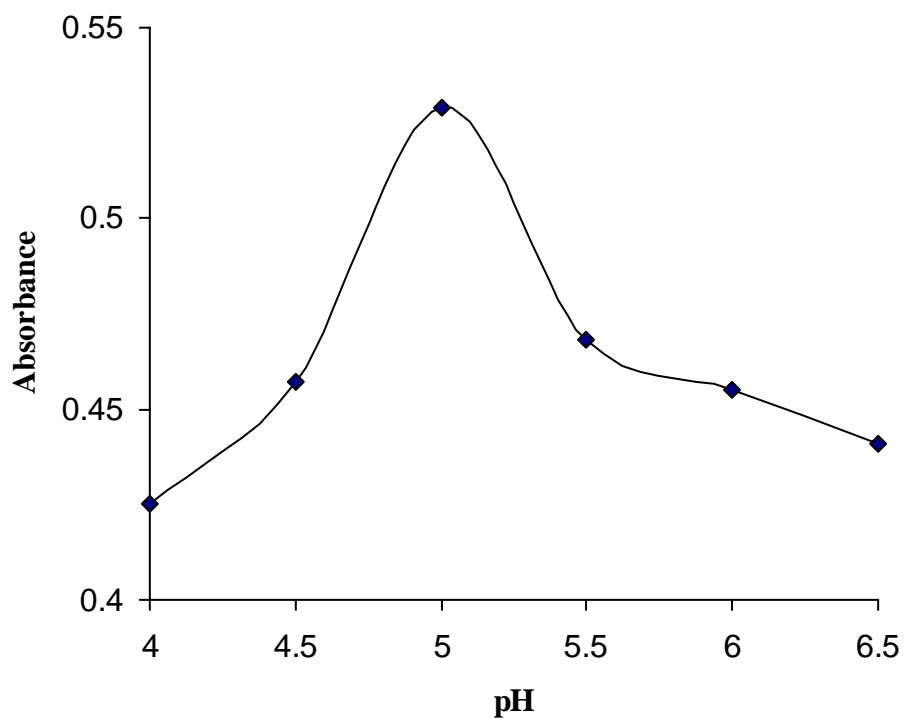


Figure 3. Effect of pH on Al-aluminon-CPC-system

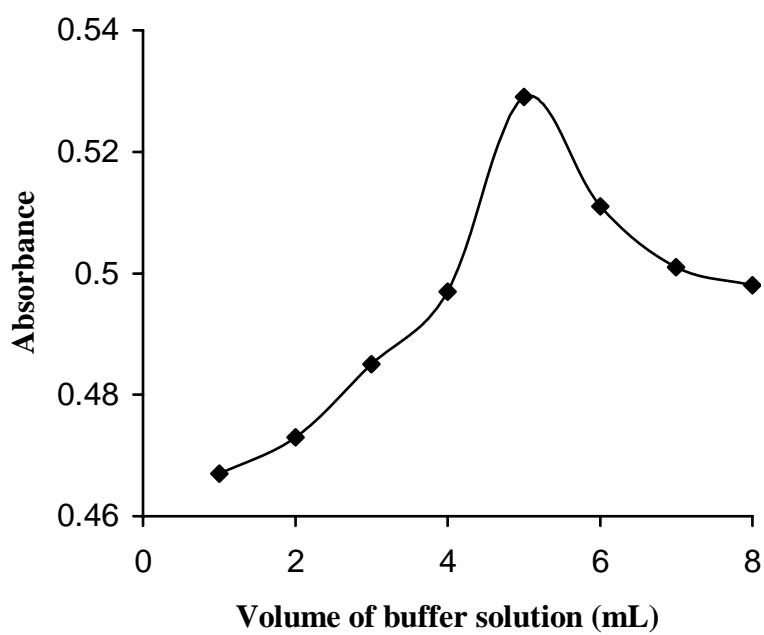


Figure 4. Effect of various volume (in mL) of acetate buffer solution of pH 5.0 on the absorbance

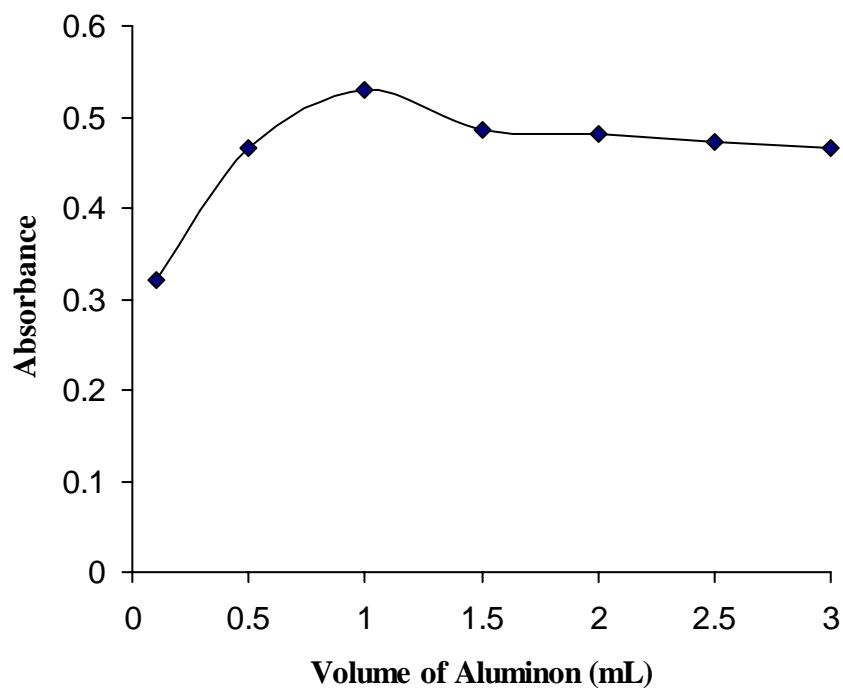


Figure 5. Absorbance as a function of aluminon concentration (mL of 0.02 mol L^{-1})

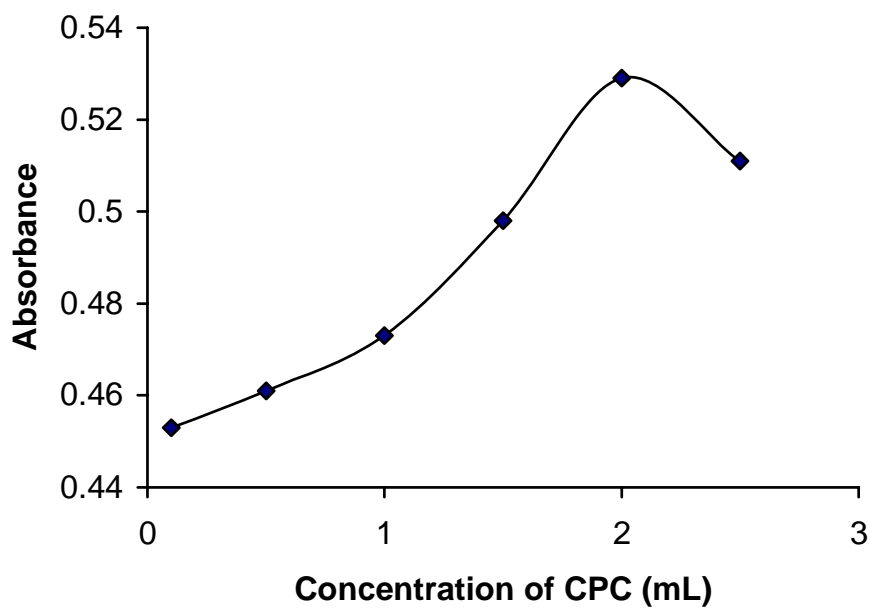


Figure 6. Effects of various volume of $1.0 \times 10^{-2} \text{ M}$ CPC on the absorbance of Al-aluminon-CPC complex.

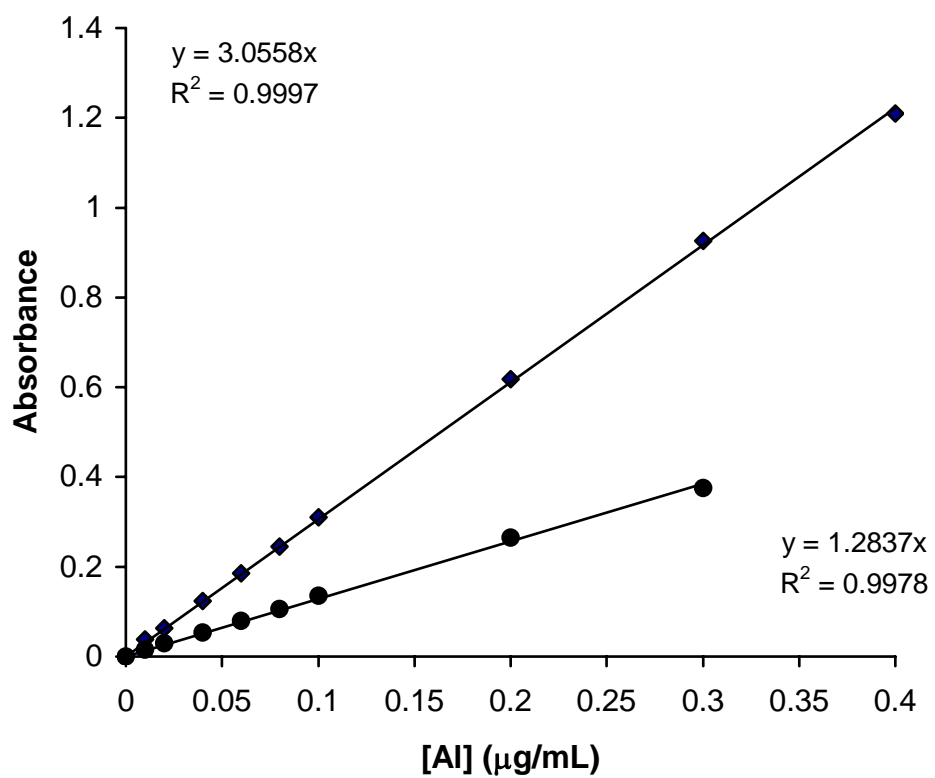


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$\text{Al}^{3+} = 9.0 \mu\text{g}$; Aluminon = 0.5 mL of 0.01 mol L^{-1}
CPC = 1.0 mL of 0.01 mol L^{-1} ; buffer solution = 5.0 mL

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Table 1. Characteristics of Al-Aluminon complex in the absence and presence of CPC

Parameter	Absence of CPC	Presence of CPC
Wave length (λ , nm)	525	535
Reaction medium (acetate buffer)	pH 3.7-5.6	pH 5.0
Stability of the complex (h)	12	24
Beer's law range ($\mu\text{g mL}^{-1}$)	0.01-0.3	0.01-0.4
Molar extinction coefficient ($\text{L mol}^{-1} \text{cm}^{-1}$)	3.46×10^4	8.24×10^4
Sandell's sensitivity (ng cm^{-2})	0.8	0.3
Regression Equation	$Y=1.2837X$	$Y=3.0558X$
Correlation Coefficient	0.997	0.9997
Relative Standard Deviation (%) (for $0.20 \mu\text{g mL}^{-1} \text{Al}^{3+}$, n=5)	--	3.1

Table 2. Effect of foreign ions on the absorbance of Al^{3+} ($0.18 \mu\text{g mL}^{-1}$) using the optimum conditions of the proposed method.

Ions	Absorbance	% Deviation
Nil	0.564	--
Cr^{+3}	0.571	1.2
Pb^{+2}	0.578	2.5
Ni^{+2}	0.591	4.7
Mg^{+2}	0.589	4.4
Ca^{+2}	0.577	2.3
Co^{+2}	0.581	3.0
Zn^{+2}	0.588	4.2
Ba^{+2}	0.592	4.9
Fe^{+3}	0.599	6.2
Ag^{+1}	0.601	6.5
Th (VI)	0.583	3.9
Nitrate	0.587	3.7
Carbonate	0.602	6.7
Thiocyanate	0.592	4.9
Iodide	0.586	3.9
Chloride	0.587	4.0
Perchlorate	0.574	1.8
Sulfate	0.571	1.2

Table 3 Determination of Aluminum in water and pharmaceutical samples

S. No	Matrices	Added (μg)	Found (μg)	Recovery (%)
1	Tap water (Muzaffarabad city)	3.0	2.86	95.3
2		6.0	4.92	98.4
3	River water, Jehlum river	3.0	2.82	94.0
4		4.5	4.42	98.2
5		6.0	5.87	97.8
6	Neelum river	4.5	4.38	97.3
7		6.0	5.85	97.5
8		9.0	8.76	97.3
Pharmaceutical Formulations				
		Present method (n=3)	FAAS method (n=3)	
9	ALUMICO (Suspension) (Regent Laboratories, Pakistan)	15.6 \pm 0.65 (mg/mL)	16.2 \pm 0.6 (mg/mL)	
10	ACTAL (Tablet) (Pharmatec Pakistan)	216 \pm 6 (mg)	218 \pm 3 (mg)	
11	GASNIL (Tablet) (Davis Pharmaceutical Laboratories, Pakistan)	246 \pm 5 (mg)	248 \pm 3 (mg)	