



Spectrophotometric determination of aluminium and indium with 2,2',3,4-tetrahydroxy-3',5'-disulphoazobenzene

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ABSTRACT

2,2',3,4-Tetrahydroxy-3',5'-disulphoazobenzene (tetrahydroxyazon 2S) has been synthesized for the first time. This reagent has been used for the spectrophotometric determination of aluminium and indium ions. The method is very sensitive and selective for the direct determination of aluminium and indium. The optimum pH and absorbance of complexes formed of tetrahydroxyazon 2S with aluminium and indium are 5; 500 nm and 495 nm for Al and In, respectively. The system obeys Beer's law at 0.05–1.6 $\mu\text{g mL}^{-1}$ of aluminium and 0.06–2.1 $\mu\text{g mL}^{-1}$ of indium concentration. The molar absorptivity is $6.42 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ for aluminium and $7.70 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ for indium. The molar compositions of the complexes are 1:1 at optimum conditions. Alkaline and alkaline earth elements, halogens, thiourea, ascorbic acid, Cd(II), Pb(II), Mn(II), Zn(II), Co(II), Ni(II), Cr(III), Bi(III), La(III), Si(IV) do not interfere this method. The method can be applied to the direct spectrophotometric determination of trace amounts of aluminium in steel, alloys, waste water, river waters, spring water and ground water. The method was also successfully applied to the indium determination in artificial mixture.

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1. Introduction

The development of the new determination methods is among the subject of the analytical chemists. For this reason extensive research has been focused on the developing sensitivity, relative simplicity, accurate, speed and costly effective methods for determination of metals which have industrial importance and affect human health. Although, none of the Group 13 elements qualifies as essential to life, aluminium and indium are of large biological interest.

Aluminium is of great concern due to its large natural abundance and its possible toxic effects [1–7]. Aluminium is the third most abundant element at the Earth's crust. It is commonly found in living organism consumed as food by human beings. The naturally occurring forms are usually stable and do not interfere with biological processes. Although, excessive use of aluminium preparations influences negatively the human organism causing disturbances in calcium and phosphate metabolism and resulting in damage to the bone system. In addition, accumulation of considerable aluminium amounts in the brain is observed in Alzheimer disease, as well senescence symptoms and amnesia of young people [8]. Therefore, the determination of trace aluminium is very important and

during the last 20 years, there are many investigations in this area [9–16].

Indium is of interest for their widespread medical and radiodiagnostic applications [17–19]. Indium is used as a semiconductor and because of its high plasticity, low melting point and relative stability, it is extensively used in non-ferrous metallurgical industries [20]. Increasing interest and importance of these metals in different fields has made it necessary to develop simple and selective methods for their determination [20].

Several techniques such as atomic absorption, atomic fluorescence, X-ray fluorescence, voltammetric, electrothermal atomic absorption or inductively coupled plasma mass spectrometry, gas chromatography have been used for the determination of aluminium in different samples [21–26]. Spectrophotometric methods are widely used due to their simplicity, rapidity, low costs and wide applications [27–29]. UV spectrophotometry amongst the optical methods seems to be most appropriate analytical approach for the determination of toxic metals, as it provides sensitive, precise and accurate measurement of suitable analytes. Besides, visible spectrophotometric detection is much more viable as useful technique to develop a portable, on-line or at-line system [30].

Many spectrophotometric methods have been proposed using various azo dyes and other chromogenic reagents such as aluminium, xylol orange, stilbazo, chlorophosphonazo I, methylthymol blue, erichrome cyanine R, chrom azurol KS, pyrocatechol violet, 8-hydroxyquinoline and alizarine [31–39] for the determination

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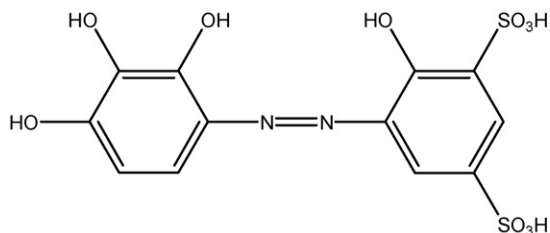


Fig. 1. 2,2',3,4-Tetrahydroxy-3',5'-disulphoazobenzene (tetrahydroxyazon 2S).

of aluminium. However, most of these methods lack sensitivity or selectivity, the procedures are sometimes rather complicated because of the need for extraction to separate interfering ions or expensive surfactants. Similarly, bromo-oxine, pyridylazoresorcinol (PAR), 1-(2-pyridylazo)-2-naphthol (PAN) have been used for spectrophotometric determination of indium. But, these reagents are less sensitive ($\epsilon = 8.8 \times 10^3$, 4.3×10^4 , 1.9×10^4 , respectively) [32].

Monoazo systems were successfully used for the determination of some metals [32,40–43]. These reagents enhance the stability of the formed band with the metals, because of high electron density between the –OH groups ortho to azo group and nitrogen atom of the azo group. For this purpose, the new method has been developed for the determination of aluminium and indium with tetrahydroxyazon 2S which have synthesized by us and the method has been applied to the determination of aluminium in certified steel, alloys, waste water, river waters, spring water and ground water samples.

The structure of the reagent is given in Fig. 1.

2. Experimental

2.1. Apparatus

The absorbance spectra were taken by Shimadzu 2101 Double beam UV–Visible spectrophotometer equipped with a quartz cell of 1.0 cm path length. The pH measurements were taken by Corning 350 pH meter.

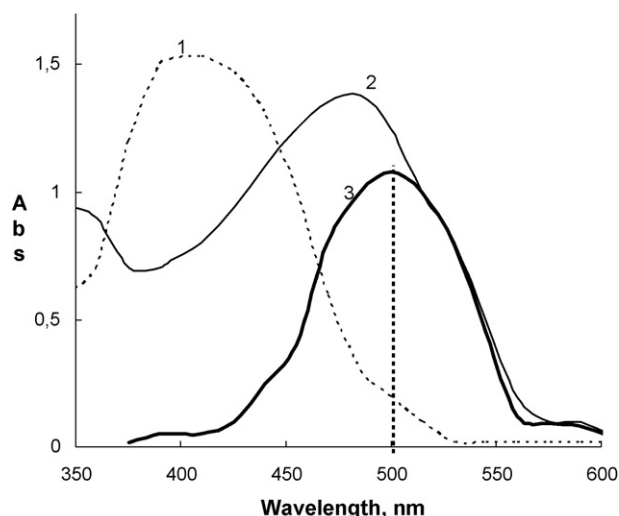


Fig. 2. The UV–vis spectra of (1) the tetrahydroxyazon 2S (blank water), (2) aluminium–tetrahydroxyazon 2S (blank water), and (3) aluminium–tetrahydroxyazon 2S complex (blank reagent); $C_{Al} = 2.0 \times 10^{-5}$ M, $C_L = 1.2 \times 10^{-4}$ M, pH 5.

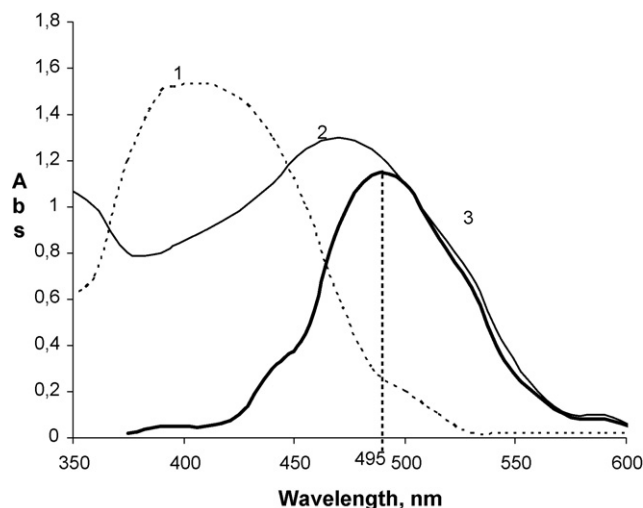


Fig. 3. The UV–vis spectra of (1) the tetrahydroxyazon 2S (blank water), (2) indium–tetrahydroxyazon 2S (blank water), and (3) indium–tetrahydroxyazon 2S complex (blank reagent); $C_{In} = 1.2 \times 10^{-5}$ M, $C_L = 1.2 \times 10^{-4}$ M, pH 5.

2.2. Chemicals

All the reagents employed were analytical grade and the solutions were prepared with bi-distilled deionized water.

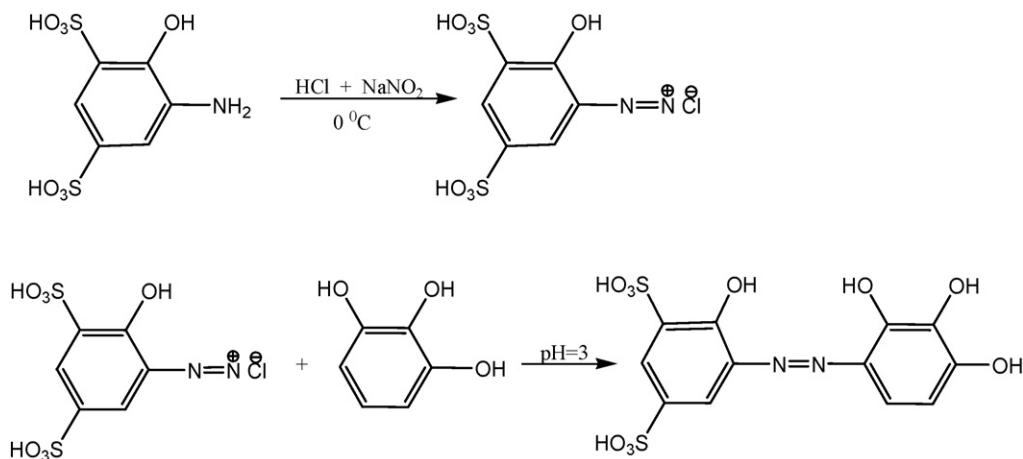
Aluminium and indium solutions (ICP 1000 mg L⁻¹, Merck) were used as a stock solution. All the working solutions were prepared by diluting appropriate volumes of the stock solution.

Tetrahydroxyazon 2S was synthesized by us and this procedure is given in “Section 2.3”. The reagent solution was prepared by dissolving 0.2032 g tetrahydroxyazon 2S in 500 mL deionized water. The solution is stable for a month, at ambient temperature.

pH 3–9 buffer solutions were prepared by ammonia and acetic acid solutions while pH 1–2 solutions were made with 0.1 and 0.01 M HCl.

2.3. Synthesis of tetrahydroxyazon 2S

The synthesis of tetrahydroxyazon 2S reagent was carried out as follows: In a three-necked 500 mL flask was placed 26.9 g (0.1 mol) 2-aminophenol-4,6-disulphonic acid and dissolved by the addition of 10 mL HCl ($d = 1.19$ g mL⁻¹) and 50 mL water. The mixture was stirred mechanically in an ice/water bath until its temperature came down to 0 °C. Meanwhile 6.9 g (0.1 mol) NaNO₂ salt was dissolved in 10 mL water and added dropwise to this flask at 0 °C in a time span of 40–50 min. After completion of the addition, the mixture was stirred for 2 h. The degree of diazotation was checked with starch paper. The excess NaNO₂ was removed by the addition of urea crystals. 13.9 g (0.11 mol) pyrogallol was dissolved separately in 50 mL water in a three-necked 25 mL flask to azotization reaction. The pH of the solution was adjusted to 3 with HCl. The mixture was cooled down to 0 °C in an ice bath, and diazonium salt containing mixture was added to it in 30 min as shown in Scheme 1. The final mixture was stirred with a mechanical stirrer for 2 h. The mixture was transferred into a 500 mL beaker and after the addition of 10 mL concentrated HCl it was kept on the bench for 12 h. The precipitate formed was filtered off with a Buchner funnel, dried in air, recrystallized from ethanol twice and kept in a desiccator. The purity of the ligand was checked with thin layer chromatography. The yield of the reaction with regard to pyrogallol was 72%, decomposed at 188 °C, elemental analysis for C₁₂H₁₀O₁₀S₂N₂: found (%) C 34.78; H 2.64; N 7.01; calculated (%) C, 35.46; H, 2.48; N, 6.89. Moreover, ultraviolet spectrum, infrared spectrum, ¹H NMR and



Scheme 1. Synthesis of tetrahydroxyazon 2S.

^{13}C NMR were also applied to study on the structure of the reagent, the results confirmed the proposed structure of tetrahydroxy 2S molecule.

2.4. General procedure

Transfer 1.25–40 μg Al^{3+} solution into a 25 mL calibrated flask. Add 3 mL 1.0×10^{-3} M tetrahydroxyazon 2S and dilute to the mark with pH 5 buffer solution. Measure the absorbance at 500 nm against the reagent blank.

Transfer 1.5–52.5 μg In^{3+} solution into a 25 mL calibrated flask. Add 3 mL 1.0×10^{-3} M tetrahydroxyazon 2S and dilute to the mark with pH 5 buffer solution. Measure the absorbance at 495 nm in a 1.0 cm cell against the reagent blank.

3. Results and discussion

3.1. Absorption spectra

The UV–vis spectra of aluminium–tetrahydroxyazon 2S and indium–tetrahydroxyazon 2S complexes were given against water and ligand (Figs. 2 and 3). The aluminium–tetrahydroxyazon 2S complex gave maximum absorbance at 500 nm, and indium–tetrahydroxyazon 2S complex gave maximum absorbance at 495 nm. The reagent showed a minimum absorbance at maximum absorbance of the complexes. Therefore, all the spectral measurements of the complexes have been carried out at 500 nm and 495 nm.

3.2. Determination of tetrahydroxyazon 2S dissociation constants

pH-metric titration in an aqueous solution was used to determine the dissociation constant of the reagent. The volume of 1.5×10^{-3} M solutions in the analysis was 50 mL. The ionic strength ($I = 0.1$) was maintained at a constant by adding a calculated amount of NaCl. A 0.1795 M solution of NaOH, free of carbon dioxide, was the titrant. The dissociation constants of the reagent were calculated by the equation presented in Ref. [44]. Tetrahydroxyazon 2S has six acidic groups in aqueous solution. However, the zero proton level was chosen as the disulfonate (H_4L^{2-}) because of the very weak acidity of the phenolic $-\text{OH}$ group. According to the calculations, $\text{p}K_1 = 3.23 \pm 0.05$, $\text{p}K_2 = 6.18 \pm 0.07$, $\text{p}K_3 = 9.04 \pm 0.03$. $\text{p}K_4$ has not been measured. This could be attributed to fourth dissociation of the reagent may be very weak. Based on these data, a diagram of the reagent distribution in the solution was plotted (Fig. 4).

It is known that the reagent form in the solution depends on the medium acidity. To determine the reagent form involved in the complexation, we used the known equations presented in Ref. [45].

It can be seen from Fig. 4 that in complexation with tetrahydroxyazon 2S, the reactive forms of the reagent are H_4L^{2-} , H_3L^{3-} and H_2L^{4-} ; their concentrations at pH 5 are 1.6, 92.3 and 6.1%, respectively.

3.3. Effect of pH

It is well known that the acidity of the medium has an important effect on complexation. The variations of the absorbances of the

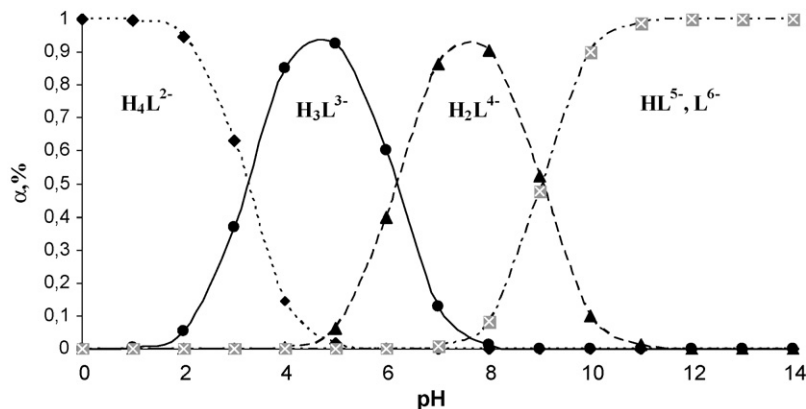


Fig. 4. Diagram of tetrahydroxyazon 2S distribution in the solution.

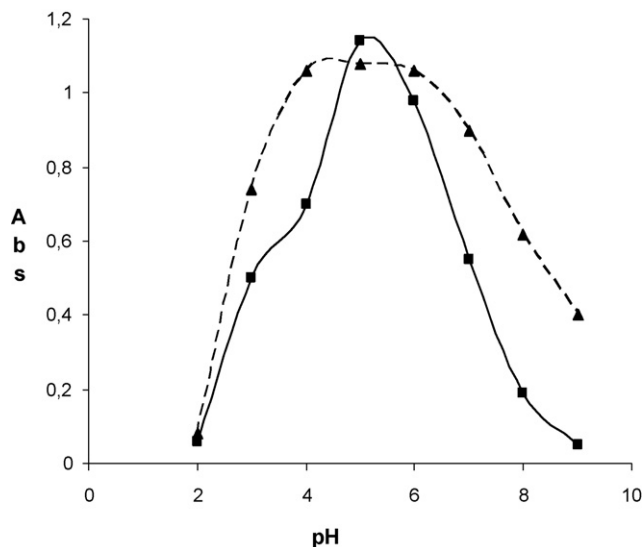


Fig. 5. The variation of the absorbance of the aluminium–tetrahydroxyazon 2S and indium–tetrahydroxyazon 2S complex vs. pH at 500 and 495 nm, respectively, $C_{Al} = 2.0 \times 10^{-5}$ M, $C_{In} = 1.2 \times 10^{-5}$ M, $C_L = 1.2 \times 10^{-4}$ M, blank reagent.

Table 1

Comparison of effect of interfering ions on the determination of aluminium and indium with tetrahydroxyazon 2S at pH 5, 500 nm and 495 nm, respectively

Interfering species (I)	Limiting mass ratio (Al:I)	Limiting mass ratio (In:I)
K ⁺	1:3000	1:1700
Na ⁺	1:3000	1:1700
Mg ²⁺	1:3000	1:800
Be ²⁺	1:3000	1:800
Sr ²⁺	1:740	1:800
Ba ²⁺	1:740	1:250
Zn ²⁺	1:540	1:400
Pb ²⁺	1:250	1:400
Ni ²⁺	1:450	1:400
Fe ²⁺	1:678	1:400
Mn ²⁺	1:250	1:400
Cu ²⁺	1:540	1:400
Cr ³⁺	1:260	1:370
Hg ²⁺	1:470	1:90
Sb ⁵⁺	1:92	1:100
Ge ⁵⁺	1:61	1:20
Zr ⁴⁺	1:23	1:20
W ⁶⁺	1:30	1:25
F ⁻	1:4000	1:800
Cl ⁻	1:4000	1:800
Br ⁻	1:4000	1:800
I ⁻	1:4000	1:800
Si ⁴⁺	1:170	–
Sn ²⁺	1:100	–
Co ²⁺	1:300	–
V ⁵⁺	1:28	–
Bi ³⁺	1:200	–
La ³⁺	1:200	–
Cd ²⁺	1:500	–
Nb ²⁺	–	1:20
Mo ⁶⁺	–	1:25
Sulphosalicylic acid	–	1:750
Urea	–	1:1000
SCN ⁻	1:2500	–
Thiourea	1:2500	–
Thiosulphate	1:2500	–
Ascorbic acid	1:4000	1:1500
Fe ³⁺ + ascorbic acid	1:602	1:412
Fe ³⁺	1:0.5	1:0.4

$C_{Al} = 2.0 \times 10^{-5}$ M, $C_{In} = 1.2 \times 10^{-5}$ M, $C_L = 1.2 \times 10^{-4}$ M.

Table 2

Determination of aluminium in water samples ($n = 5$, $p = 0.95$), pH 5, 500 nm

Sample	Aluminium (mg/L)		R.S.D.% ^a	AAS method, $\bar{X} \pm (ts/\sqrt{n})$
	Added	Found, $\bar{X} \pm (ts/\sqrt{n})$		
Waste water		0.150 ± 0.007	0.038	0.156 ± 0.005
River water-1	4.000	4.080 ± 0.004	0.031	4.110 ± 0.006
River water-2		0.120 ± 0.005	0.028	0.130 ± 0.007
Spring water	6.000	6.250 ± 0.003	0.039	6.210 ± 0.006
Ground water		0.018 ± 0.003	0.042	0.021 ± 0.005

^a R.S.D.% = $\frac{s}{\bar{X}} \times 100$.

Table 3

Determination of aluminium in standard steel and alloy samples^a ($n = 5$, $p = 0.95$) pH 5, 500 nm

Steel samples	Aluminium (%)		R.S.D.% ^b
	Certified	Found, $\bar{X} \pm (ts/\sqrt{n})$	
Medium carbon steel 221	0.036	0.035 ± 0.005	0.043
Steel 223a	0.420	0.450 ± 0.004	0.032
Steel 380	0.024	0.026 ± 0.005	0.045
Steel 102	0.229	0.228 ± 0.003	0.034
Alloy 951	0.050	0.057 ± 0.007	0.038
Alloy M223x	1.360	1.354 ± 0.005	0.026

^a Medium carbon steel 221: C: 0.37; Si: 0.282; Mn: 0.67; S: 0.005; P: 0.013; Cr: 0.189; Cu: 0.14; Ni: 0.202; N: 0.0105; Co: 0.014; Sn: 0.012, Steel 223a: Mn: 0.34; Ni: 0.17; Cr: 1.68; Cu: 0.15; W: 0.33; V: 0.17, Steel 380: Mn: 0.266; Ni: 0.042; Cu: 0.102; Cr: 0.037; Si: 0.058; P: 0.0046; S: 0.017, Steel 102: P: 0.022; As: 0.012; S: 0.031; C: 0.217; Cr: 0.212; V: 0.006; Mn: 0.917; Ni: 0.105; Ti: 0.002; Cu: 0.243; Mo: 0.018, Alloy 951: Fe: 0.005; Pb: 0.006; Cd: 0.002; Cu: 0.003; Sb: 0.002; Sn: 0.001, Alloy M223x: P: 0.022; As: 0.012; S: 0.031; C: 0.217; Cr: 0.212; V: 0.006; Mn: 0.917; Ni: 0.105; Ti: 0.002; Cu: 0.243; Mo: 0.018.

^b R.S.D.% = $\frac{s}{\bar{X}} \times 100$

aluminium–tetrahydroxyazon 2S and indium–tetrahydroxyazon 2S complexes were investigated in a wide pH range. The obtained results are given in Fig. 5. These two complexes give a maximum absorbance at pH 5

3.4. Effect of the ligand concentration

In the case of the addition of the increased concentrations of tetrahydroxyazon 2S to aluminium solution, the absorbance of aluminium–tetrahydroxyazon 2S complex increased and became constant in the 1.2×10^{-4} M of tetrahydroxyazon 2S at 500 nm. For this reason, the present study was carried out with the 1.2×10^{-4} M of tetrahydroxyazon 2S concentration. Indium complex also gave maximum absorbance in 1.2×10^{-4} M of ligand concentration.

3.5. Effect of the temperature and standing time

The aluminium immediately formed the complex with tetrahydroxyazon 2S, and the absorbance of this complex remained constant for 24 h and the complex was stable up to 80 °C. The indium–tetrahydroxyazon 2S complex remained constant for 12 h and the complex was stable up to 60 °C.

Table 4

Determination of indium in artificial mixture ($n = 5$, $p = 0.95$) pH 5, 495 nm

Sample	Composition of mixture $\mu\text{g}/25$ mL	Indium, $\mu\text{g}/25$ mL	
		Added	Found, $\bar{X} \pm (ts/\sqrt{n})$
I	In	10.000	9.960 ± 0.030
I	Asc. Ac. ^a + In + (300) Pb ²⁺ + (300) Fe ³⁺	10.000	10.030 ± 0.040
II	Asc. Ac. ^a + In + (500) Ni ²⁺ + (500) Fe ³⁺	10.000	10.060 ± 0.060

^a Asc. Ac. = Ascorbic acid.

Table 5
Comparison of some reagent characteristics for spectrophotometric determination of aluminium reported in the literature

Reagent	pH	λ_{\max} (nm)	ϵ (L mol ⁻¹ cm ⁻¹)	L. R. ($\mu\text{g/mL}$)	Remarks	Ref.
Bis-(2,3,4-trihydroxyphenylazo)benzidine	4.8–5.3	445	11.2×10^3	0.054–0.648	(1) Cu ²⁺ , Zr ⁴⁺ , V ⁵⁺ , F ⁻ , thiourea are interfere; (2) required adding another reagent for increasing selectivity	[12]
Eriochrome cyanine R	5.0	584	1.19×10^5	0.004–0.400	(1) Required using cationic surfactant for increasing sensitivity	[39]
Tetrahydroxyazon SN	4.0	479	5.46×10^4	0.005–1.079	(1) Ni ²⁺ , Zn ²⁺ , Co ²⁺ are interfere	[41]
Semi-xyleneol orange	2.6	526	3.30×10^4	0.080–0.800	(1) Required adding another reagent for increasing selectivity; (2) temperature influence on the reaction rate	[48]
Trimethoxyphenylfluorone	0.9	506	2.02×10^4	0.002–0.050	(1) Required using cationic surfactant for increasing sensitivity; (2) time influence on the reaction rate	[49]
3,5-Ditertbutylsalicylfluorone	5.0–10.0	542	3.52×10^6	NR	(1) Required doing extraction for increasing sensitivity and selectivity; (2) required using cationic surfactants for increasing sensitivity	[50]
Chrome azurol S	6.0	380	NR	0.003–0.100	(1) Required using cationic surfactants for increasing sensitivity	[51]
Tetrahydroxyazon 2S	5.0	500	6.42×10^4	0.050–1.600	(1) Do not required using cationic surfactants; (2) do not require doing extraction; (3) temperature and time do not influence on the reaction rate; (4) highly sensitive and selective	PM

PM: present method, NR: not reported.

3.6. Calibration curve

Under the optimum conditions given in Section 2.4. Absorbances of the complexes obey Beer's law in the aluminium ion concentration range of 0.05–1.6 $\mu\text{g mL}^{-1}$ and indium ion concentration range of 0.06–2.1 $\mu\text{g mL}^{-1}$. The molar absorption coefficients of aluminium and indium were found as $6.42 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $7.70 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$, respectively.

3.7. Effect of interfering species

In order to assess the possible analytical applications of these color reactions, the effect of some foreign ions is examined, by carrying out determinations of $2.0 \times 10^{-5} \text{ M}$ ($0.54 \mu\text{g mL}^{-1}$) of aluminium(III) and $1.2 \times 10^{-5} \text{ M}$ ($1.38 \mu\text{g mL}^{-1}$) indium(III) with a known amount of foreign ion solution, using the recommended analytical procedure. An error of $\pm 4\%$ in absorbance reading is considered tolerable. The results are given in Table 1. Fe(III) interference was masked by using ascorbic acid.

3.8. Composition of the complex

The molar compositions of the complexes were studied using Job's method of continuous variation, Asmus method [46] and mole-ratio methods. These methods indicated a 1:1 ratio of complexes may be formed aluminium and indium with tetrahydroxyazon 2S.

4. Applications

4.1. Determination of aluminium in industrial waste water

A 200 mL of industrial waste water sample was evaporated up to the 10–15 mL in sand bath and then 10 mL concentrated HCl added. This solution was cooled down and diluted to 50 mL with deionized water. A 2–6 mL of it was taken into 25 mL graduated flask for analysis. After additions of 3 mL of 0.1 M ascorbic acid (in order to reduction of Fe³⁺ into Fe²⁺) and 3 mL of $1.0 \times 10^{-3} \text{ M}$ tetrahydroxyazon 2S reagent, the solution was neutralized and diluted to mark with pH 5. The absorbance of the solution was measured at 500 nm. Analysis of results of aluminium in water samples are given in Table 2. The results are in reasonable agreement with those determined by the atomic absorption spectrometry (AAS).

4.2. Determination of aluminium in water samples

The river, spring, ground and sea water samples (1000 mL) were evaporated nearly to dryness with mixture of 1 mL concentrated H₂SO₄ and 5 mL HNO₃ in a fume cupboard and was then heated with 10 mL of deionized water in order to dissolve the salts. The solution was then cooled and neutralized with dilute NH₄OH. The resulting solution was then transferred into a 25 mL calibrated flask and diluted with deionized water.

An aliquot 2 mL of this preconcentrated water samples was pipetted into a 25 mL calibrated flask and the aluminium content was determined. The sample solutions were appropriately diluted for spectrophotometric determination. Interference of Fe(III) could be eliminated by masking with ascorbic acid. Table 2 shows that there is no significant difference between proposed method and AAS method.

4.3. Determination of aluminium in steels and alloys

In order to evaluate the accuracy of the developed procedure, aluminium was determined in a reference material, supplied by Baku of Steel Company. A 0.5003 g of aluminium based alloys or steels were taken into a 250 mL beaker and the method proposed by Mendham et al. [47] was applied to dissolve these samples. These solutions are prepared as in literature [43]. A 2–6 mL of these solutions were taken into 25 mL graduated flask for analysis. After additions of 3 mL of 0.1 M ascorbic acid (in order to reduction of Fe³⁺ into Fe²⁺) and 3 mL of the aqueous solution $1.0 \times 10^{-3} \text{ M}$ tetrahydroxyazon 2S reagent, the solution was neutralized and diluted to mark with pH 5. The absorbance of the solution was measured at 500 nm. The amount of Al(III) in the certified alloys or steels was determined by the use of the calibration curves. The result is summarized in Table 3 and no significant difference between achieved results by the proposed method and certified values was found. It demonstrated also that there is no significant difference among the achieved results and the certified values for a confidence level of 95%.

4.4. Determination of indium in artificial mixture

The method was successfully applied to the indium determination in artificial mixture. The mixtures were prepared as follows:

- (I) Ascorbic acid + (10 μg) indium + (300 μg) Pb²⁺ + (300 μg) Fe³⁺
- (II) Ascorbic acid + (10 μg) indium + (500 μg) Ni²⁺ + (500 μg) Fe³⁺

These mixtures were transferred into 25 mL calibrate flask and diluted with pH 5. The absorbances of colored solutions were measured at 495 nm. The results were given in Table 4. The proposed method has high accuracy and precision.

5. Conclusion

In this work, a new azo dye, tetrahydroxyazon 2S, was synthesized, and a new UV–vis spectrophotometric method was developed for the determination of aluminium and indium. Alkaline, earth alkaline elements, rare earth elements, halides, ascorbic acid, Cu^{2+} , Co^{2+} , Pb^{2+} , Ni^{2+} , Zn^{2+} , Fe^{2+} , Cr^{3+} , Mn^{2+} , Hg^{2+} , Sn^{2+} , Cd^{2+} , Bi^{3+} , La^{3+} , Si^{4+} and Sr^{2+} , did not interfere in this method. Molar absorptivities of the complexes are $6.42 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $7.70 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$, for aluminium and indium, respectively. The stoichiometries of complexes were found 1:1 in the optimum conditions. The system obeys Beer's law in the range of $0.05\text{--}1.6 \mu\text{g mL}^{-1}$ for aluminium and $0.06\text{--}2.1 \mu\text{g mL}^{-1}$ for indium.

The proposed method has a very high selectivity, and nearly all of the anions and most of the cations do not interfere with the chromogenic reaction.

This new reagent does not need to use some surfactants for enhancement of selectivity and sensitivity of the method and does not require using some separation techniques like extraction. When compared to the reported spectrophotometric methods in Table 5.

As conclusion the proposed simple, reproducible, easy and sensitivity method for the determination of aluminium different samples such as water, certificated steels and alloys can be used successfully.

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References

- [1] R.A. Yokel, The toxicology of aluminum in the brain: a review, *Neurotoxicology* 21 (2000) 813–828.
- [2] C. Exley, E. Burgess, J.P. Day, E.H. Jeffrey, S. Melethil, R.A. Yokel, Aluminum toxicokinetics, *J. Toxicol. Environ. Health* 48 (1996) 569–584.
- [3] T.P. Flaten, A.C. Alfrey, J.D. Birchall, J. Savory, R.A. Yokel, Status and future concerns of clinical and environmental aluminum toxicology, *J. Toxicol. Environ. Health* 48 (1996) 527–541.
- [4] R.A. Yokel, Aluminum chelation-chemistry, clinical and experimental studies and the search for alternatives to desferrioxamine, *J. Toxicol. Environ. Health* 41 (1994) 131–174.
- [5] B. Corani, G.G. Bombi, A. Tapparo, M. Nicolini, P. Zatta, M. Perazzolo, M. Favarato, Alzheimers-disease and aluminum toxicology, *Environ. Health Perspect.* 89 (1990) 233–235.
- [6] H.M. Wisniewski, G.Y. Wen, *Aluminum in Biology and Medicine*, Wiley, New York, 1992.
- [7] J. Fleming, J.G. Joshi, Ferritin-isolation of aluminum ferritin complex from brain, *Proc. Natl. Acad. Sci. U.S.A.* 84 (1987) 7870–7876.
- [8] S. Zareba, J. Melke, Spectrophotometric determination of aluminium in pharmaceutical preparations by azo dyes of 1,2,4-triazole series, *Pharma. Acta Helv.* 74 (2000) 361–364.
- [9] J. Tria, E.C.V. Butler, P.R. Haddad, A.R. Bowie, Determination of aluminium in natural water samples, *Anal. Chim. Acta* 588 (2007) 153–165.
- [10] H.L. Zheng, W.Q. Xiong, Y.K. Gong, D.J. Peng, L.C. Li, Catalytic spectrophotometric determination of trace aluminium with indigo carmine, *Spectrochim. Acta Part A* 66 (2007) 1243–1247.
- [11] A. Safavi, H. Abdollahi, R. Mirzajani, Simultaneous spectrophotometric determination of Fe(III), Al(III) and Cu(II) by partial least-squares calibration method, *Spectrochim. Acta Part A* 63 (2007) 196–199.
- [12] R.A. Alieva, F.S. Alieva, F.M. Chyragov, Bis-(2,3,4-trihydroxyphenylazo)-benzidine as a reagent for the photometric determination of aluminum, *J. Anal. Chem.* 61 (2006) 630–633.
- [13] L. Zajjun, L. Naping, Z. Xia, S. Qijun, Extraction spectrophotometric determination of aluminum in dialysis concentrates with 3,5-ditertbutylsilylfluorone and ionic liquid 1-butyl-3-trimethylsilylimidazolium hexafluorophosphate, *J. Pharm. Biomed. Anal.* 43 (2007) 1609–1614.
- [14] D.G. Themelis, F.S. Kika, Flow and sequential injection methods for the spectrofluorimetric determination of aluminium in pharmaceutical products using chromotropic acid as chromogenic reagent, *J. Pharm. Biomed. Anal.* 41 (2006) 1179–1185.
- [15] J.L. Rodrigues, C.S. Magalhaes, P.O. Luccas, Flow injection spectrophotometric determination of Al in hemodialysis solutions, *J. Pharm. Biomed. Anal.* 36 (2005) 1119–1123.
- [16] T. Madrakian, A. Afkhami, M. Borazjani, M. Bahram, Partial least-squares regression for the simultaneous determination of aluminum and beryllium in geochemical samples using xylenol orange, *Spectrochim. Acta Part A* 61 (2005) 2988–2994.
- [17] M.J. Abrams, B.A. Murrer, Metal-compounds in therapy and diagnosis, *Science* 261 (1993) 725–730.
- [18] L.R. Bernstein, Mechanisms of therapeutic activity for gallium, *Pharmacol. Rev.* 50 (1998) 665–682.
- [19] P.G.H.M. Raijmakers, A.B.J. Groeneveld, W. Den Hollander, G.J.J. Teule, Transport of ga-67 and in-111 across a membrane—role of plasma-binding and concentration gradients, *Nucl. Med. Commun.* 13 (1992) 349–356.
- [20] J.L. Bernal, M.J. Del Nozal, L. Deban, A.J. Aller, Determination of indium in aluminum-alloys by flame atomic-absorption spectroscopy and flame atomic-emission spectrometry, *Talanta* 29 (1982) 1113–1116.
- [21] S.B. Gündüz, S. Küçükolbaşı, O. Atakol, E. Kılıç, Spectrofluorimetric determination of trace aluminum in diluted hemodialysis solutions, *Spectrochim. Acta Part A* 61 (2005) 913–921.
- [22] K.B. Pierson, M.A. Evonson, Measurement of aluminum in neuronal tissues using electrothermal atomization atomic-absorption spectrophotometry, *Anal. Chem.* 58 (1986) 1744–1748.
- [23] S. Hirata, Y. Umezaki, M. Ikeda, Determination of chromium(III), titanium, vanadium, iron(III), and aluminum by inductively coupled plasma atomic emission-spectrometry with an online preconcentrating ion-exchange column, *Anal. Chem.* 58 (1986) 2602–2606.
- [24] T. Korenaga, S. Motomizu, K. Toei, Modified extraction procedure for the spectrophotometric determination of trace amounts of aluminum in sea-water with pyrocatechol violet and removal of excess of reagent, *Analyst* 105 (1980) 328–332.
- [25] J. Di, S. Bi, T. Yang, M. Zhang, Voltammetric determination of aluminum(III) using a reagentless sensor fabricated by sol-gel process, *Sens. Actuators B: Chem.* 99 (2004) 468–473.
- [26] G. Albendin, M.P. Manuel-Vez, C. Moreno, M. Garcia-Varas, Reverse flow-injection manifold for spectrofluorimetric determination of aluminum in drinking water, *Talanta* 60 (2003) 425–431.
- [27] A.R. Fakhari, A.R. Khorrami, H. Naeimi, Synthesis and analytical application of a novel tetradentate N_2O_2 Schiff base as a chromogenic reagent for determination of nickel in some natural food samples, *Talanta* 66 (2005) 813–817.
- [28] H. Filik, E. Tütem, R. Apak, E. Erçağ, Spectrophotometric determination of gallium(III) with carminic acid and hexadecylpyridinium chloride, *Microchim. Acta* 129 (1998) 57–63.
- [29] S.A. Reddy, K.J. Reddy, S. Lakshminarayana, D.L. Priya, Y.S. Rao, A.V. Reddy, Extractive spectrophotometric determination of trace amounts of cadmium(II) in medicinal leaves and environmental samples using benzilidithiosemicarbazone (BDTSC), *J. Hazard. Mater.* 152 (3) (2008) 903–909.
- [30] S. Suresha, M.F. Silwadi, A.A. Syed, Sensitive and selective spectrophotometric determination of Hg(II), Ni(II), Cu(II) and Co(II) using iminodibenzyl and 3-chloroiminodibenzyl as new reagents and their applications to industrial effluents and soil samples, *Int. J. Environ. Anal. Chem.* 82 (5) (2002) 275–289.
- [31] Z. Ying-Quan, Z. Lin, L. Jun-Yi, Spectrophotometric determination of aluminium with chlorophosphonazo I, *Talanta* 30 (1983) 291–293.
- [32] Z. Marczenko, *Spectrophotometric Determination of Elements*, Wiley, New York, 1976.
- [33] S. Tagashira, Distribution equilibria of aluminum pyrocatechol violet quaternary onium salt ion-pairs in micellar systems—spectrophotometric determination of aluminum, *Anal. Chim. Acta* 157 (1984) 343–348.
- [34] C. Martire, L. Hainberger, Sensitive and selective spectrophotometric determination of aluminum with chrome fast pure blue-b and cetyltrimethylammoniumbromide, *Mikrochim. Acta* 11 (1985) 223–229.
- [35] C. Wyganowski, S. Motomizu, K. Toei, Spectrophotometric determination of aluminum with bromopyrogallol red and a quaternary ammonium salt—determination of aluminum in river water, *Mikrochim. Acta* 1 (1983) 55–64.
- [36] L. Shao-pu, Highly sensitive spectrophotometric determination of trace amounts of aluminium with chromazol KS and cetylpyridinium bromide, *Analyst* 107 (1982) 428–432.
- [37] M. Chamsaz, M.H. Arbab Zavar, M.S. Hosseini, Flotation spectrophotometric determination of aluminum with alizarin, *Anal. Lett.* 33 (8) (2000) 1625–1633.
- [38] J.M. Samaritan, J.D. Wehr, M.A. Buccafuri, M. Sahn, Automated measurement of aqueous aluminum by the pyrocatechol violet method, *Int. J. Environ. Anal. Chem.* 50 (3) (1993) 173–182.
- [39] A. Shokrollahi, M. Ghaedi, M.S. Niband, H.R. Rajabi, Selective and sensitive spectrophotometric method for determination of sub-micro-molar amounts of aluminium ion, *J. Hazard. Mater.* 151 (2/3) (2008) 642–648.
- [40] S.M.Z. Al-Kindy, S.S. Al-Ghamari, F.E.O. Suliman, A sequential injection method for the fluorimetric determination of aluminum in drinking water using 8-hydroxy-7-(4-sulfo-1-naphthylazo)-5-quinoline sulfonic acid, *Spectrochim. Acta Part A* 68 (2007) 1174–1179.

- [41] T. Güray, U.D. Uysal, A.A. Huseyinli, T. Gedikbey, 2,2',3,4-tetrahydroxy-3'-sulpho-5'-nitroazobenzene for spectrophotometric determination of aluminium in pharmaceutical suspensions and granite, *Anal. Chim. Acta* 545 (2005) 107–112.
- [42] A.A. Huseyinli, A. Atılır, Determination of toxic elements in some natural samples, *Toxicology* 164 (2001) 229.
- [43] A.A. Huseyinli, F. Köseoğlu, U.D. Uysal, Rapid spectrophotometric determination of zirconium(IV) with 2,2',3,4-tetrahydroxy-3'-sulpho-5'-chloroazobenzene in alloys, *Anal. Sci.* 17 (ICAS2001) i793–796.
- [44] N.M. Dyatlova, V.Ya. Temkina, I.D. Kolpakova, *Kompleksyony (Complexones)*, Khimiya, Moscow, 1970.
- [45] E.N. Dorokhova, G.V. Prokhorova, *Zadachi i voprosy po analiticheskoi khimii (Exercises in Analytical Chemistry)*, Mir, Moscow, 2001.
- [46] E. Asmus, Determination of the composition of weak complexes, *Z. Anal. Chem.* 178 (1960) 104–109.
- [47] J. Mendham, R.C. Denney, J.D. Barnes, M. Thomas, *Vogel's Textbook of Quantitative Chemical Analysis*, 6th ed., Prentice-Hall, London/New York/Toronto, 2000, p. 473.
- [48] Z. Nan, Selective spectrophotometric determination of aluminium in the presence of beryllium and lanthanide cations, *Microchim. Acta* 146 (2004) 73–78.
- [49] J.R. Ren, T. Zeng, J.R. Li, J.X. Yang, H.W. Gao, Determination of aluminium ion at ng mL^{-1} level in natural water using trimethoxyphenylfluorone by light-absorption ratio variation approach, *Can. J. Anal. Sci. Spectr.* 51 (2006) 24–34.
- [50] L. Zaijun, L. Naping, Z. Xia, S. Qijun, Extraction spectrophotometric determination of aluminium in dialysis concentrates with 3,5-ditertbutylsalicylfluorone and ionic liquid 1-butyl-3-trimethylsilylimidazolium hexafluorophosphate, *J. Pharm. Biomed. Anal.* 43 (2007) 1609–1614.
- [51] M. Bahram, T. Madrakian, E. Bozorgzadeh, A. Afkhami, Micelle-mediated extraction for simultaneous spectrophotometric determination of aluminium and beryllium using mean centring of ratio spectra, *Talanta* 72 (2007) 408–414.