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Synthesis and spectrophotometric determination of acidity constants of 2,3,4,6′-tetrahydroxy-3′-sulfoazobenzene and their use in determination of aluminum

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A novel azo derivative, 2,3,4,6′-tetrahydroxy-3′-sulfoazobenzene (THSA), was synthesized by using pyrogallol. The acid dissociation constants, or K_a values, of THSA were determined by the UV-visible spectroscopic technique. The protonation and deprotonation behaviors of the title molecule were studied from the super basic to the super acid region (i.e. 10 N NaOH to 98% H_2SO_4), including the pH region. A selective and sensitive UV-visible spectrophotometric method was devised for determination of aluminum by using this ligand. The developed method was successfully applied to an alunite mineral and to pharmaceutical preparations for the determination of aluminum.

Key Words: Azo dye, acidity constants, aluminum, spectrophotometric determination

Introduction

Azo compounds are still a very important class of chemical compounds receiving much attention in scientific research due to their chromophoric properties and fine staining qualities. These compounds have been commonly used in both industry and analytical chemistry.[1,2] In particular, 2,2′-dihydroxyazo compounds are well known

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for their applications in analytical chemistry as chromogenic indicators.[3–5] They are also being used for the spectrophotometric determination of metal ions.[6–10]

Recently, tetrahydroxyazobenzene derivatives have started to be used in spectrophotometric determination of aluminum.[9,10] These reagents enhance the stability of the formed band with the aluminum because of the high electron density between the –OH groups' ortho to azo group and the nitrogen atom of the azo group.

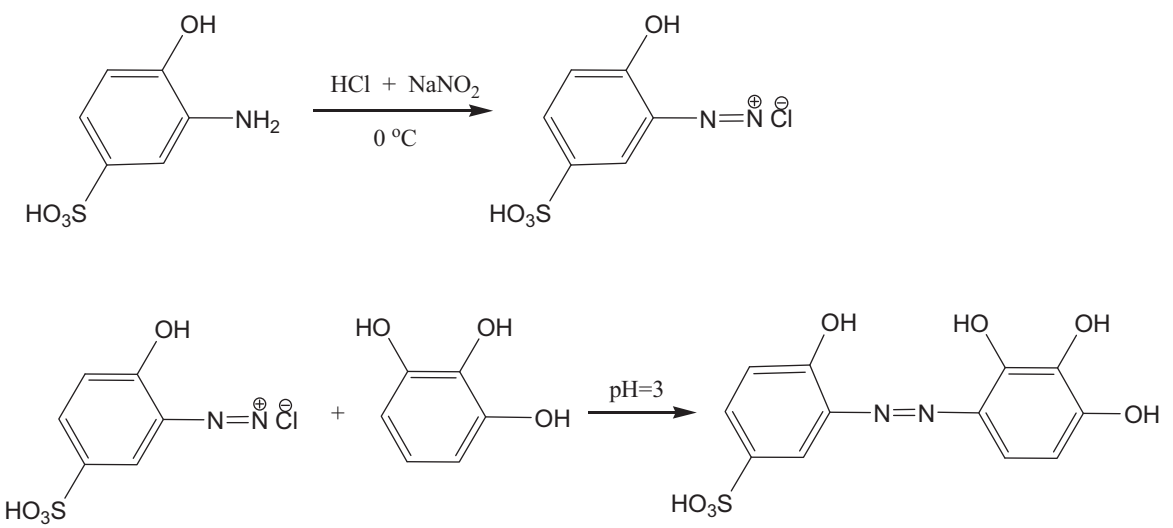
Most of the commonly used reagents for the determination of aluminum in the literature do not have high sensitivity[11] or require some surfactants for the enhancement of selectivity and sensitivity.[12,13]

During the last 20 years, many investigators have focused on the toxicity of aluminum to living systems.[14,15] Furthermore, aluminum is widely used as an antiperspirant in both cosmetic and pharmaceutical products. Scientists are currently investigating suggestions of a link between the use of deodorants and both breast cancer and Alzheimer's disease.[16–18]

Commonly used analytical techniques for the determination of aluminum at trace levels are fluorimetry,[19] atomic absorption spectroscopy (AAS),[20] emission spectroscopy (AES),[21] gas chromatography,[22] and inductively coupled plasma atomic emission spectrometry (ICP-AES).[23]

The knowledge of the pK_a value of a substance is essential for various investigations in pharmacology and physiology, for industrial purposes, in structural, environmental, preparative, and analytical studies, and so on. Hence, we have determined the acidity constants of THSA by the spectrophotometric method. Spectrometry is an ideal method[24] when a substance is not soluble enough for potentiometry or when its acidity constant value is particularly low or high (i.e. less than 2 or greater than 11).

In the present work, we have synthesized a novel THSA (Scheme 1). We are now reporting on the determination of the acidity, which is expressed as acidity constants, or pK_a values. We also report on the usage of this reagent in the spectrophotometric determination of aluminum in artificial mixtures, alunite mineral, and pharmaceutical preparations.



Scheme 1. Synthesis of THSA.

Experimental

Instrumentation

The spectrophotometric measurements were carried out using a Unicam 2-UV Spectrometer Double Beam UV-Visible spectrophotometer with a 1.00-cm quartz cell. The pH measurements were taken using an Orion 720A pH meter.

Materials

The THSA was synthesized as in the literature.[8] A stock solution of THSA was prepared by dissolving 0.1631 g of THSA in 500 mL of deionized water. The solution was stabilized for 1 month.

KOH, H_2SO_4, HCl, CH_3COOH, CH_3COONa, NaOH, KH_2PO_4, Na_2CO_3, $NaHCO_3$, NaCl, and standard buffer solutions were obtained from Merck and were not purified further.

Acid solutions were prepared with H_2SO_4 (w/w, 0.0049%-98% H_2SO_4) in water.[25] The CO_2-free NaOH solutions were prepared with NaOH pellets (1-16.4 mol L^{-1}) in water.[26] Buffer solutions were prepared using Perrin's descriptions.[27] The potentiometric measurements were performed by measuring the hydrogen ion concentration under nitrogen atmosphere at 25 ± 0.1 °C, and ionic strengths of the media were maintained at 0.1 M using NaCl.

An alunite sample was obtained from Şaphane, Kütahya, Turkey. It was crushed, powdered, and sieved through a 150-μm sieve, and samples were collected. The chemical composition of the alunite as determined by XRF analysis was 43.47% silica, 27.12% alumina (14.386% aluminum), 23.50% sulfur trioxide, and 5.50% potassium oxide as the major constituents, along with 0.41% of other compounds as impurities.[28]

A commercial preparation of oxethazaine [Mucaine® suspension containing 291 mg of aluminum hydroxide (100.656 mg of aluminum) in 5 mL] was obtained from Wyeth (İstanbul, Turkey), a commercial preparation of dihydroxyaluminum sodium carbonate (DASC) [Kompensan® tablet containing 340 mg of DASC (54.970 mg of aluminum) in 1 tablet (1 g)] was obtained from Pfizer (İstanbul, Turkey), and aluminum solution (ICP 1000 mg L^{-1}, Merck) was used as a stock solution. All solutions were prepared by diluting appropriate volumes of the stock solution.

Synthesis of THSA

The THSA was synthesized using a recommended method from the literature.[8] In a 3-necked, 250-mL flask was placed 4.725 g (0.025 mol) of 2-aminophenol-4-sulfonic acid, dissolved by the addition of 5 mL of HCl (d = 1.19 g mL^{-1}) and 50 mL of water. The mixture was stirred mechanically in an ice-water bath until its temperature dropped to 0 °C. Meanwhile, 1.725 g (0.025 mol) of $NaNO_2$ salt was dissolved in 5 mL of water and added dropwise to the flask at 0 °C within 30 min. After completion of the addition, the mixture was stirred for 2 h. The degree of diazotization was checked with starch paper. The excess $NaNO_2$ was removed by the addition of urea crystals, and 3.2 g (0.0255 mol) of pyrogallol was dissolved separately in 20 mL of water in a 3-necked, 25-mL flask for the azotization reaction. The pH of the solution was adjusted to 3 with HCl. The mixture was cooled to 0 °C in an ice bath, and a mixture containing diazonium salt was added to it within 30 min

(Scheme 1). The final mixture was stirred with a mechanical stirrer for 2 h. The mixture was transferred to a 250-mL beaker, and after the addition of 5 mL of concentrated HCl, it was kept on the bench for 1 night. The crude product was chloride salt. The precipitate formed was filtered off with a Büchner funnel, air-dried, 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 47.8%, decomposed at >200 °C. Elemental analysis for $C_{12}H_{10}O_7N_2S$: Found (%) C 44.04, H 2.95, N 8.10; Calculated (%) C 44.17, H 3.09, N 8.59. Moreover, the ultraviolet spectrum, infrared spectrum, ^{1}H-NMR, and ^{13}C-NMR were also applied for structure elucidation.

Spectrophotometric determination of acidity constants of THSA

The general procedure was applied as follows: a stock solution of the compound under investigation was prepared by dissolving about 10-20 mg of the compound in water in a volumetric flask. Aliquots (1 mL) of this solution were transferred to 10-mL volumetric flasks and diluted to the mark with buffers of various pH values. The pH was measured before and after addition of the new solution. The optical density of each solution was then measured in 1-cm cells, against solvent blanks, using a constant temperature cell holder Unicam UV2 UV-Vis scanning spectrometer thermostated at 25 ± 0.1 °C. The wavelength was chosen such that the fully protonated form of the substrate had a much greater or a much smaller extinction coefficient than the neutral form. The analytical wavelengths, the half-protonation values, and the UV absorption maximum are shown in Tables 1 and 2.

This method depends on the direct determination of the ratio of the concentration of molecular species, that is, the neutral molecules corresponding to the ionized species in a series of nonabsorbing buffer solutions for which pH values are either known or measured.[24,29] For a weak base B, which ionizes by simple proton addition, the H_o, H_-, or pH values at half-protonation were measured during the course of the present work using the UV-Vis spectrophotometric method of Johnson et al.[30] This method takes into account any effect of the medium on the wavelength of the maximum UV absorption and the corresponding extinction coefficient. This effect is particularly significant at high acidities. The protonation of a weak base can be defined as follows:[25]

$$HX + SH \rightleftharpoons X^- + SH_2^+, \tag{1}$$

where SH is the solvent.

Calculations of half-protonation values were carried out as follows: the sigmoid curve of optical density or the extinction coefficients at the analytical wavelength (OD, λ) were first obtained (Figure 1). The optical density of the fully protonated molecule (OD_{ca}, optical density of conjugated acid) and the pure free base (OD_{fb}, optical density of free base) at an acidity were then calculated by linear extrapolation of the arms of the curve. The following equation, Eq. (2), gives the ionization ratio in which the OD_{obs} (the observed optical density) is in turn converted into molar extinction, ε_{obs}, using Beer's law of OD = $\varepsilon.b.c$ (b= cell width, cm; c = concentration, mol L^{-1}):

$$I = (HX)/(X^-) = (OD_{obs} - OD_{fb})/(OD_{ca} - OD_{obs}) = (\varepsilon_{obs} - \varepsilon_{fb})/(\varepsilon_{ca} - \varepsilon_{obs}). \tag{2}$$

Table 1. UV spectral data and acidity constants, pK_a values, of THSA for the first and second protonation.

	ε_{max}			log ε			$H^{1/2d}$	m^e	pK_a	λ^f_{max} (nm)	R^{2g}
	ε_{max} (Neutral)^a	ε_{max} (Monocation)^b	ε_{max} (Dication)^c	log ε (Neutral)^a	log ε (Monocation)^b	log ε (Dication)^c					
First Prot.	8440	24,857.14	-	3.93	4.40	-	6.10	1.02	6.25	469	0.99
Second Prot.	-	8388.57	34,552.73	-	3.92	4.54	-0.61	-0.44	2.27	469	0.98

[a]Measured in pH 7 buffer solution. [b]Measured in pH 1 buffer solution. [c]Measured in 98% H_2SO_4. [d]Half-protonation value. [e]Slope of log I-pH (or H_o) graphs. [f]A wavelength of the measurement. [g]Correlations for log Ias a function of pH (or H_o) graph.

Table 2. UV spectral data and acidity constants, pK_a values, of THSA for the first and second deprotonation.

	ε_{max}			log ε			$H^{1/2d}$	m^e	pK_a	λ^f_{max} (nm)	R^{2g}
	ε_{max} (Neutral)^a	ε_{max} (Monocation)^b	ε_{max} (Dication)^c	log ε (Neutral)^a	log ε (Monocation)^b	log ε (Dication)^c					
First Deprot.	24240	18400	-	4.38	4.26	-	8.20	0.67	5.49	469	0.99
Second Deprot.	-	24857	4120	-	4.40	3.61	13.64	0.42	5.77	469	0.98

[a]Measured in pH 7 buffer solution. [b]Measured in pH 1 buffer solution. [c]Measured in 98% H_2SO_4. [d]Half-protonation value. [e]Slope of log I-pH (or H_o) graphs. [f]A wavelength of the measurement. [g]Correlations for log$I$as a function of pH (or H_o) graph.

The linear plot of log I against H_o or pH, using the values -1.0 < log I < 1.0, had slope m, yielding a half-protonation value of $H^{1/2}$ or $pH^{1/2}$ at log $I = 0$ (Figure 1). The pK_a values were calculated by using Eq. (3):

$$pK_a = H^{1/2} + logI, \tag{3}$$

which can mathematically be expressed as a straight line ($y = mx + n$) with a slope of m, thus becoming Eq. (4).

$$pK_a = m \cdot H^{1/2} + logI \tag{4}$$

Since at the half-protonation point, log I will be equal to 0, we end up with Eq. (5):

$$pK_a = m \cdot H^{1/2}. \tag{5}$$

As the half-protonation value is equal to pK_a in the pH region, pK_a is equal to the $H^{1/2}$ value of 6.10.

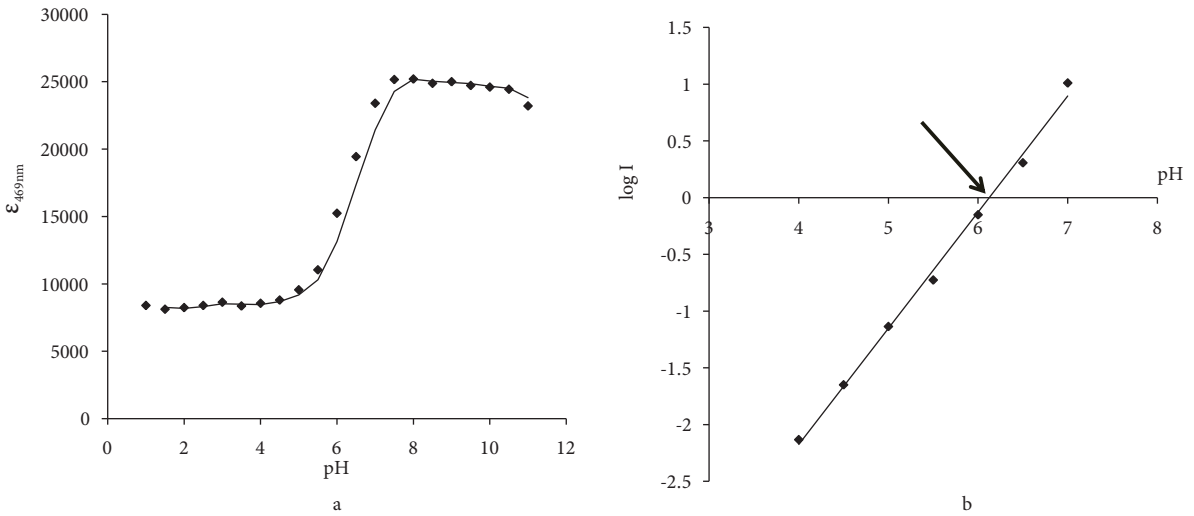


Figure 1. a) The sigmoid curve pH-ε_{469} nm plot. **b)** The log I − pH plot for THSA for the first protonation (R^2 = 0.99).

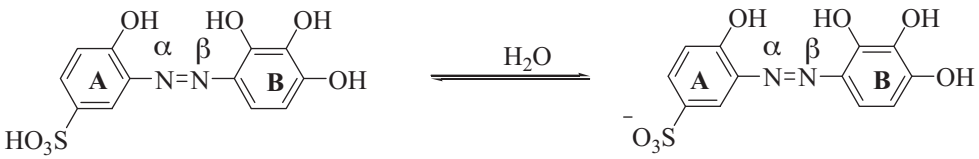
General procedure for determination of aluminum

An aluminum solution (5×10^{-4} mol L^{-1}) was transferred into a 25-mL calibrated flask. THSA (2 mL of 1×10^{-3} mol L^{-1}) was then added to this solution, and the colored solution was diluted with appropriate solutions of pH 1-11. The final concentrations of aluminum and THSA in the reaction mixture were 2×10^{-5} mol L^{-1} and 8×10^{-5} mol L^{-1}, respectively. The absorbances were measured by using either a blank reagent or water at 480 nm.

Result and discussion

The protonation and deprotonation behaviors of the THSA

UV-Vis spectroscopic data related to the deprotonation and protonation processes of THSA are depicted in Tables 1 and 2. Possible protonation patterns are shown in Schemes 2, 3, 4, and 5. The obtained results will be discussed using the scale of Scheme 6.



Scheme 2. Ionization of sulfonate group in THSA.

Deprotonation in the sulfonate group is very acidic and not detectable in the pH range of determination (Scheme 2).

pH 7-pH 1 region: The first protonation (pK_a = 6.10) of the studied molecule presumably occurs within this slightly acidic region. The slope of 1.02 for the first protonation of THSA seems to occur at the azo (–N=N–) group (path I in Scheme 3).[31–33] The presence of 3 phenolic hydroxide groups on ring **B** at the ortho, meta, and para positions will increase the electron density on βN through mesomeric electron donation. In the THSA molecule, the electron-donating power of the *o*-hydroxyl group on ring **A** has obviously subsided, and the electron-withdrawing power of the sulfonium group comes into effect, making αN more electron-poor.

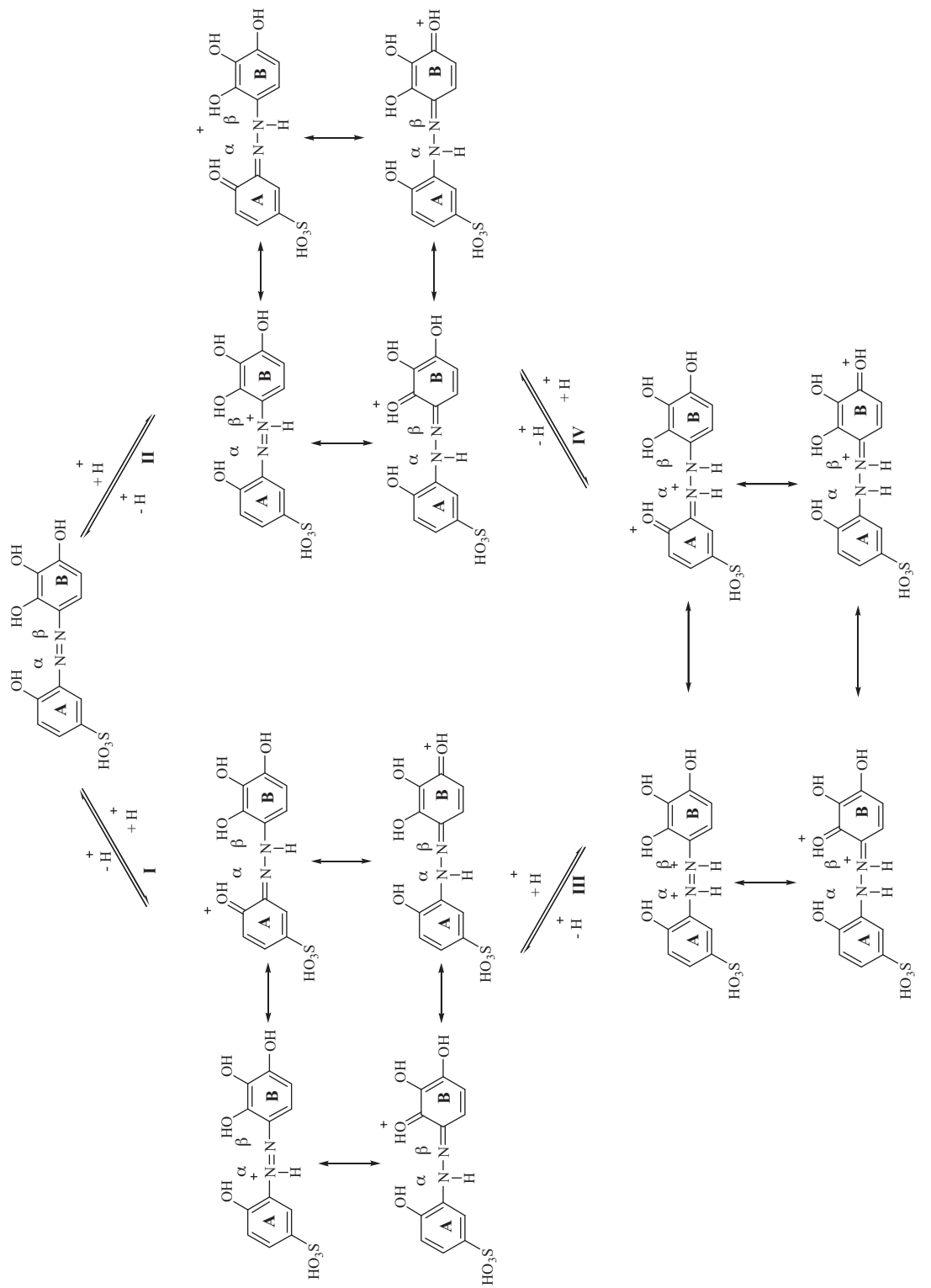
pH 1-50% H_2SO_4 region: The obtained acidity constant for this region was 0.61. The second protonation of THSA seems to occur on the second azo nitrogen atom, which is next to the quarter nitrogen atom, as depicted in Scheme 4.

0.1 N NaOH-pH 7 region: The obtained acidity constant for this region was 8.20 (path II in Scheme 5). Therefore, the first deprotonation would be possible from the p-hydroxyl group of ring **B** (a phenolic deprotonation).

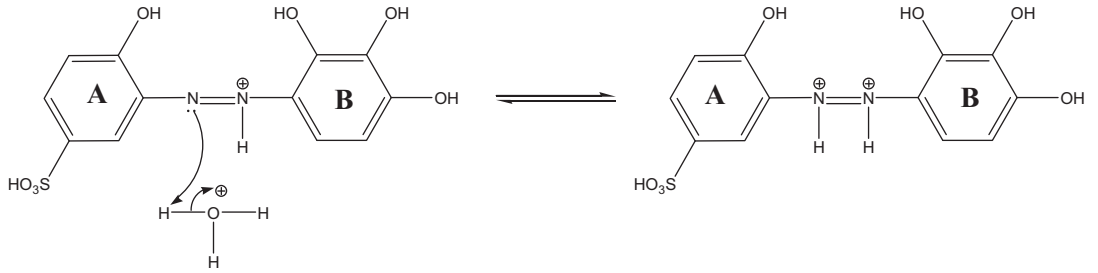
10 N NaOH-0.1 N NaOH region: The obtained acidity constant for this region was 13.64. The same situation is acceptable for the second deprotonation (path VII in Scheme 5). The second deprotonation would be possible from the o-hydroxyl group of ring **B** (a phenolic deprotonation).

Absorption spectra of aluminum-THSA complex

The UV-Vis spectrum of the aluminum-THSA complex was given against water and ligand (Figure 2). The aluminum-THSA complex showed maximum absorbance at 480 nm. The reagent showed a minimum absorbance at the maximum absorbance of the complexes. Therefore, all of the spectral measurements of the complexes were carried out at 480 nm.



Scheme 3. Possible protonation pathways for THSA.



Scheme 4. Possible second protonation for THSA.

Effect of pH

It is well known that the acidity of the medium has an important effect on complexation. The variation of the absorbance of the aluminum-THSA complex was investigated in a wide pH range. The obtained results are given in Figure 3. These show that the aluminum-THSA complex had a maximum absorbance at pH 5. For this reason, the UV-Vis spectrum of the aluminum-THSA complex was given at pH 5 against water and ligand (Figure 2).

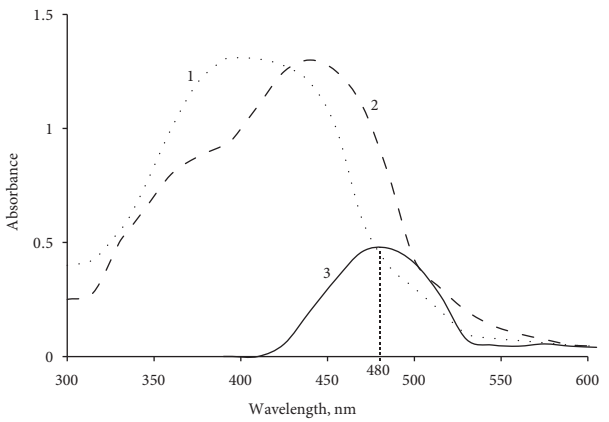


Figure 2. The UV-Vis spectra of 1) the THSA (blank water), 2) the complex (blank water), and 3) the complex (blank ligand); $C_M = 2 \times 10^{-5}$ mol L^{-1}, $C_L = 8 \times 10^{-5}$ mol L^{-1}, pH = 5.

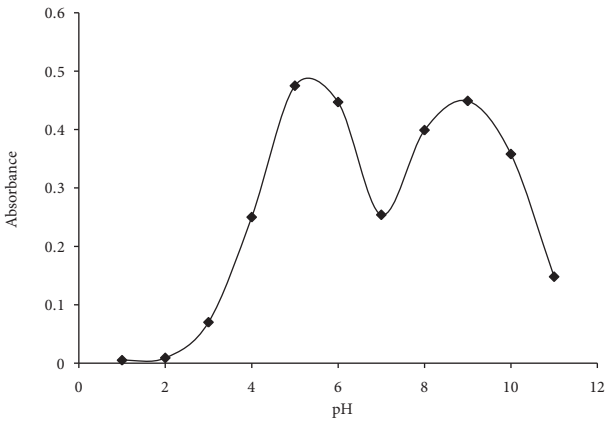
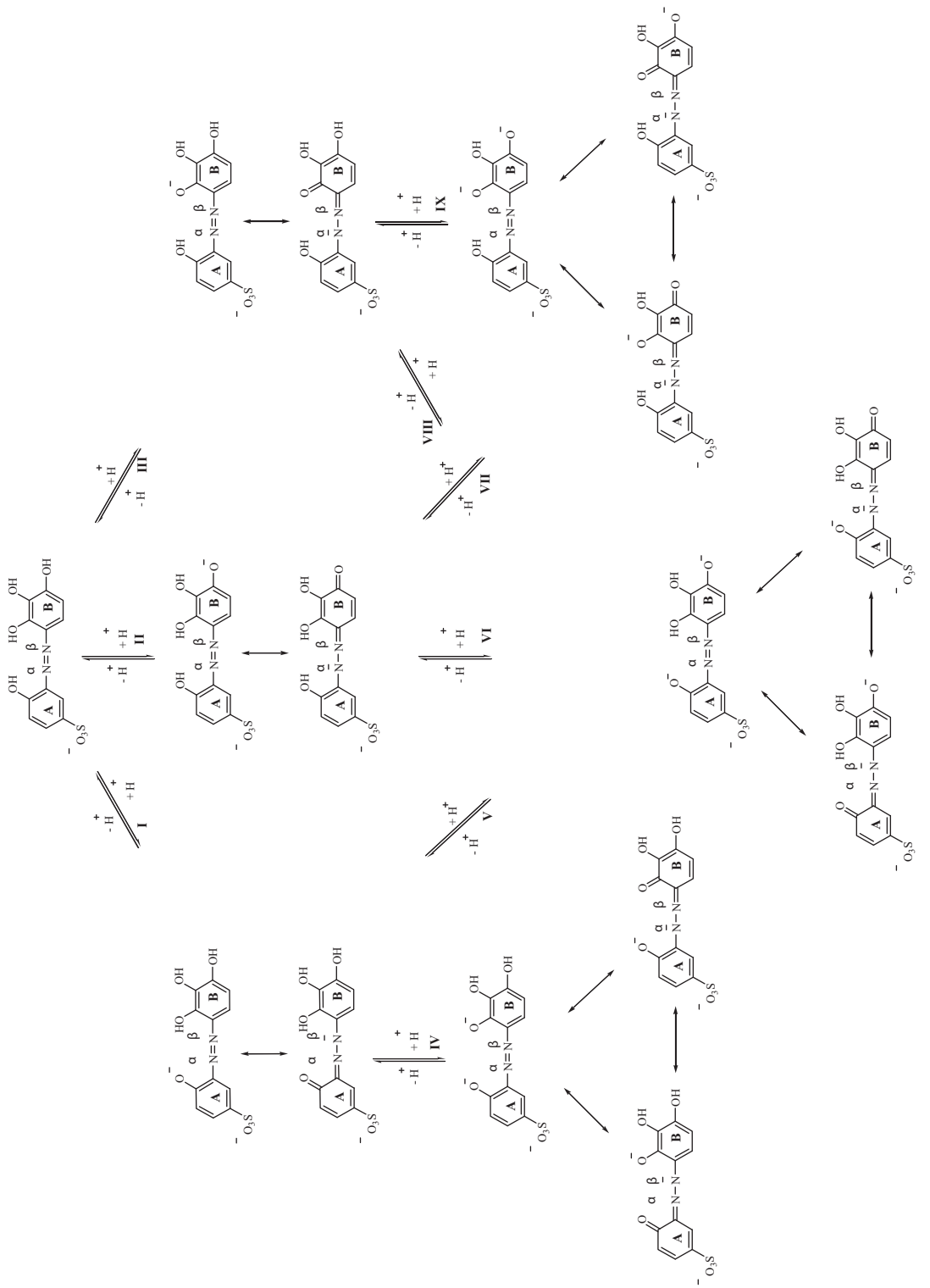


Figure 3. The variation of the absorbance of the aluminum-THSA complex versus pH at 480 nm, $C_M = 2 \times 10^{-5}$ mol L^{-1}, $C_L = 8 \times 10^{-5}$ mol L^{-1}, blank reagent.

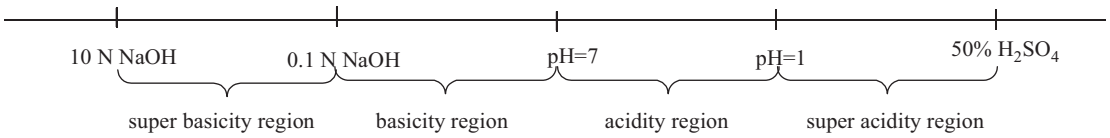
Calibration curve

Under the optimum conditions given in "General Procedure for Determination of Aluminum," the complex absorbance obeys Beer's law in the aluminum ion concentration range of 0.018-1.075 μg mL^{-1}. The molar absorption coefficient was found to be 4.17×10^4 L mol^{-1} cm^{-1}. The linear relationship between the absorbance and concentration was found to be as follows:

$$(A = 0.0312C + 0.0542, r = 0.9988).$$



Scheme 5. Possible deprotonation pathways for THSA.



Scheme 6. Used acidity scale for acidity of THSA.

Here, C is μg Al(III) 25 mL^{-1} and A is the absorbance of the complex solution.

Effect of the ligand concentration

In the case of the addition of the increased concentrations of THSA to aluminum solution, the absorbance of the aluminum-THSA complex increased and became constant in 8 $\times$ 10^{-5} mol L^{-1} THSA at 480 nm. For this reason, the present study was carried out with the 8 $\times$ 10^{-5} mol L^{-1} THSA concentration.

Effect of temperature and standing time

The aluminum immediately formed the complex with THSA, and the absorbance of this complex remained constant for 3 days. The complex was stable at up to 60 °C.

Effect of interfering species

The effect of the interfering species upon the complex was investigated by the use of the proposed method at optimum conditions. Fe(III) and Cu(II) interferences were masked by using ascorbic acid and thiourea masking agents, respectively. The results are given in Table 3.

Composition of the complex

The molar composition of the complex was studied using Job's method and the mole ratio method, which indicated a 1:1 ratio of aluminum and THSA in the complex.

Applications of the method

Determination of aluminum in artificial mixture

Some different artificial mixtures were prepared, and these mixtures were analyzed by this method. The method was successfully applied to aluminum determination in an artificial mixture. The mixtures were prepared as follows:

I- 0.5 mg aluminum + 5 mg Fe^{3+} + 1 mg Zn^{2+}

II- 0.5 mg aluminum + 5 mg Fe^{3+} + 1 mg Co^{2+}

These mixtures were transferred into 50-mL calibrated flasks and diluted with a buffer solution of pH 5. Aliquot parts of these solutions, in the range of 0.2-0.8 μg mL^{-1}, were put into a 25-mL calibrated flask. The absorbances at 480 nm were recorded according to the general procedure. It was observed that samples containing 0.2-0.8 μg mL^{-1} of aluminum ion could be analyzed with a standard deviation (s) $\leq$ 0.045 (I) and

0.039 (II) for the ion. In order to ensure the accuracy of the method, 5 replicated measurements were carried out with standard solutions containing 0.5 μg mL^{-1} (I and II) of aluminum. The accuracy was calculated from the equation of absolute value of accuracy (%):

$$|(\text{Found Al} - (\text{Spiked Al} + \text{Aliquot Al})) \times (\text{Spiked Al} + \text{Aliquot Al})^{-1}| \times 100. \quad (6)$$

The accuracy for determination was 2.40% (I) and 0.80% (II), respectively.

Table 3. Comparison of the effect of interfering species on the determination of aluminum with THSA at pH 5 and 480 nm. $C_{Al} = 2 \times 10^{-5}$ mol L^{-1}, $C_L = 8 \times 10^{-5}$ mol L^{-1}.

Interfering species (I)	Limiting mass ratio (Al:I)	Interfering species (I)	Limiting mass ratio (Al:I)
K^+	1:4000	F^-	1:100
Na^+	1:2200	Cl^-	1:2500
Mg^{2+}	1:4000	Br^-	1:6550
Pb^{2+}	1:15	I^-	1:7200
Bi^{3+}	1:25	MoO_4^{2-}	1:15
Hg^{2+}	1:100	AsO_4^-	1:100
Cd^{2+}	1:2300	$B_4O_7^{2-}$	1:125
Mn^{2+}	1:250	HPO_4^{2-}	1:1540
Cr^{3+}	1:400	SCN^-	1:2500
Sn^{2+}	1:150	Thiosulfate	1:2500
Sr^{2+}	1:700	Ascorbic acid	1:4000
Be^{2+}	1:220	Thiourea	1:2500
Si^{2+}	1:55		
Zn^{2+}	1:6		
Co^{2+}	1:6		
Ni^{2+}	1:6		
Fe^{3+} + Ascorbic acid	1:13		
Cu^{2+} + Thiourea	1:25		

Application of the method to alunite

The method was applied to an alunite mineral; 0.1002 g of alunite was put into a platinum crucible with 1 mL of $HClO_4$ and 3 mL of HF added, and the solution evaporated almost to dryness on the sand bath. After cooling, 1 mL of $HClO_4$, 1 mL of HNO_3, 2 mL of HCl, and 20 mL of distilled water were added and the solution was gently warmed until all of the salts dissolved. The solution was cooled and diluted to 100 mL.

From that solution, 1 mL was diluted to 10 mL. The aliquot part of the solution, in the range of 0.018-1.075 μg mL^{-1}, was transferred to a 25-mL calibrated flask, and then 2 mL of a 1×10^{-3} M THSA reagent was added. The obtained mixture was diluted with a buffer solution of pH 5. The absorbance of the colored solution was measured at 480 nm. The aluminum content of the alunite was 14.276 $\pm$ 1.463 (S.D. = 0.355,

R.S.D. = 2.487). The obtained result was compared with the XRF value (Al % = 14.358).[28] There was good agreement between the values obtained by the spectrophotometric method and XRF.

Application of the method to pharmaceutical preparations

Aluminum was detected in the same pharmaceutical preparations using the method described in the pharmacopeia procedures given in USP XXIV.[34]

For the analysis of aluminum, the method was applied to a Mucaine® suspension (containing 100.656 mg of aluminum in a 5-mL suspension) and a Kompensan® tablet (54.970 mg of aluminum in a 1-g tablet). A stock solution of the suspension was prepared by following the pharmacopeia procedure as given in USP XXIV.[34]

From the stock solution, 1 mL was taken and diluted to 100 mL. The aliquot part of this solution, in the range of 0.018-1.075 μg mL^{-1}, was transferred to a 25-mL calibrated flask, and 2 mL of a 1 $\times$ 10^{-3} M THSA reagent was added. The obtained mixture was diluted with a buffer solution of pH 5. The absorbance of the colored solution was measured at 480 nm.

When the proposed method was compared with the pharmacopeia procedure, high reproducibility and insignificant differences were observed at the 95% probability level (Table 4). The results ($\bar{X}$, SD, RSD%, and confidence limits (CL)) by the proposed method are in good agreement with those of the pharmacopeia procedure as given in USP XXIV.[34] General rules for the quantification of aluminum hydroxide gel were employed for the acceptance criteria. These allow for the equivalent of not less than 90.0% and not more than 110.0% of the labeled amount of aluminum hydroxide ($Al(OH)_3$) in aluminum hydroxide gel. Likewise, this rule was employed for aluminum hydroxychloride and dihydroxyaluminum sodium carbonate.

Table 4. Determination of aluminum in pharmaceutical preparations by the proposed method and the pharmacopeia procedure.

	Proposed method (n = 8)		Pharmacopeia procedure[a] (n = 8)	
	Mucaine suspension[b]	*Kompensan tablet*[c]	*Mucaine suspension*[b]	*Kompensan tablet*[c]
$\bar{X}$(mg)	99.811	53.917	101.912	55.789
$\bar{X}$ (%)	99.152	98.084	101.250	101.490
[d]S.D. (s)	1.090	2.312	2.030	3.355
[e]R.S.D. (%)	1.092	4.288	1.99	6.014
[f]CL (P = 0.05)	99.811 ± 0.911	53.917 ± 2.870	101.912 ± 1.700	55.789 ± 4.166

[a] Ref. 34, [b] Mucaine® suspension: 100.66 mg Al 5 mL suspension^{-1}, [c] Kompensan® tablet: 54.970 mg Al 1 g tablet^{-1}, [d] S.D. (s) $= \sqrt{\frac{(x_{i1}-\overline{x})^2+(x_{i2}-\overline{x})^2+.....+(x_{iN}-\overline{x})^2}{N-1}}$, [e] R.S.D. (%) $= \frac{s}{\bar{X}}.100$, [f] CL $= \bar{X} \pm \frac{ts}{\sqrt{N}}$

Conclusion

In this study, a novel azo dye, THSA, was synthesized, and we proved the feasibility of a UV-Vis spectroscopic method that uses absorbance values to determine the ionization constants of THSA in water solutions.

The new UV-Vis spectrophotometric method was developed for determination of aluminum. Earth alkaline, alkaline elements, rare earth elements, halides, phosphates, Mn^{2+}, Hg^{2+}, Sn^{2+}, Cr^{3+}, Cd^{2+}, and Sr^{2+} did not interfere in this method. Molar absorptivity of the complex was 4.17×10^4 L mol^{-1} cm^{-1}. The stoichiometry of the complex was found to be 1:1 at optimum conditions. The method obeyed Beer's law in the range of 0.018-1.075 μg mL^{-1}.

This new reagent does not require surfactants for enhancement of the selectivity and sensitivity of the method and does not require separation techniques like extraction.

This method has been successfully applied to alunite mineral and certified pharmaceutical preparations. In conclusion, the developed method is selective, sensitive, reproducible, rapid, simple, and economical. Hence, this method can be successfully applied as an alternative to existing methods for determination of aluminum.

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