

# Spectrophotometric Investigation of the Complexation Equilibria of Zirconium(IV) with *Lawson* and Determination of Zirconium

H. Sedaira

Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt

**Summary.** The complexation equilibria of zirconium(IV) with *lawson* (2-hydroxy-1,4-naphthoquinone) have been studied spectrophotometrically in 40% (v/v) ethanol at 20°C and at an ionic strength of 0.1 M (NaClO<sub>4</sub>). A complete picture of the solution equilibria in the pH range 1.5–4.0 is presented. The absorbance vs. pH graphs were analyzed to characterize the complexation equilibria in solution. A simple, rapid, selective, and sensitive method for the spectrophotometric determination of zirconium is proposed based on the formation of Zr(*lawson*)<sub>2</sub> at pH 3.3 ( $\lambda_{\max} = 450$  nm,  $\epsilon = 1.13 \times 10^4 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ). The interference caused by a number of ions can be masked by the addition of cyanide. The method has been applied to the determination of zirconium in some synthetic samples.

**Keywords.** Zirconium(IV) determination; *Lawson*; Spectrophotometry; Complex equilibria.

## **Spektrophotometrische Untersuchung der Komplexierungsgleichgewichte von Zirkonium(IV) mit *Lawson* und Bestimmung von Zirkonium**

**Zusammenfassung.** Die Komplexierungsgleichgewichte von Zirkonium(IV) mit *Lawson* (2-Hydroxy-1,4-naphthochinon) wurden spektrophotometrisch in 40%igem Ethanol (v/v) bei 20°C und einer Ionenstärke von 0.1 M (NaClO<sub>4</sub>) untersucht. Ein vollständiges Bild der Gleichgewichte in Lösung im pH-Bereich von 1.5 bis 4.0 wird präsentiert. Die Extinktions-pH-Kurven wurden analysiert, um die Komplexierungsgleichgewichte in Lösung zu charakterisieren. Eine einfache, schnelle, selektive und empfindliche Methode zur spektrophotometrischen Zirkoniumbestimmung auf der Basis der Bildung des Zr (*lawson*)<sub>2</sub>-Komplexes bei pH = 3.3 ( $\lambda_{\max} = 450$  nm,  $\epsilon = 1.13 \times 10^4 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ) wird vorgestellt. Eine Anzahl störender Ionen kann durch Zugabe von Cyanid maskiert werden. Die Methode wurde zur Zirkoniumbestimmung in einigen synthetischen Proben eingesetzt.

## **Introduction**

Alizarin sulfonate [1, 2], phenylfluorone [3], xylenol orange [4], pyrocatechol violet [5], chloranilic acid [6], bromanilic acid [7], pyridylazo dyes [8, 9], and arsenazo III [10] have been found to be useful for spectrophotometric determination of zirconium. *Idriss et al.* [11] have recently investigated the complexation

equilibria of zirconium(IV) with 1-amino-4-hydroxyanthraquinone, and a direct spectrophotometric determination of zirconium has been reported.

2-Hydroxy-1,4-naphthoquinone (*lawsone*, *LAS*) is found in the leaves of *lawsone alba* (Henna). Preparation and characterization of its solid chelates with some divalent metal ions have been reported [12–15], and the reactivity of *lawsone* towards mercury(II) has been investigated [16].

This paper describes the complexation equilibria of *LAS* with zirconium(IV). The complex species present in solution are characterized, and the fundamental conditions favouring the direct spectrophotometric determination of trace amounts of zirconium using *LAS* are reported.

## Experimental

### *Zirconium(IV) standard solution*

A stock solution of  $5 \times 10^{-3} M$  Zr(IV) was prepared by dissolving Analar zirconyl chloride octahydrate ( $ZrOCl_2 \cdot 8H_2O$ ) in 0.1 M  $HClO_4$  solution. The zirconium concentration was determined by titration with *EDTA*.

### *2-Hydroxy-1,4-naphthoquinone, Lawsone (LAS)*

A stock solution of  $5 \times 10^{-3} M$  in ethanol was prepared using the Aldrich reagent. More dilute solutions were obtained as required by accurate dilution.

### *Reagents*

Sodium perchlorate and perchloric acid standard solutions as well as solutions of foreign ions used for interference studies were prepared from analytical grade chemicals using deionized water. The acidity of the solutions investigated was adjusted by addition of either dilute perchloric acid or sodium hydroxide. The ionic strength was kept constant at  $I = 0.1 M(NaClO_4)$ .

### *Measurement conditions*

The absorption spectra were recorded on a Perkin-Elmer Lambda 3B spectrophotometer in the range of 300–600 nm using 1 cm matched quartz cells *pH* values were read from a Radiometer *pH* meter (Model M 63) equipped with a Radiometer combined glass electrode (GK 2301 C). The *pH* meter was calibrated with standard buffer solutions. All measurements were performed in the presence of 40% (v/v) spectro-grade ethanol at 20°C. *pH* values of partially aqueous solutions were corrected as described elsewhere [17].

Infrared spectra of the reagent and the solid chelates were recorded as CsBr discs on a Perkin-Elmer 251 IR spectrophotometer.

The molar conductivity of the complexes was measured using an Industrial Instruments conductance bridge (Model RC-16B2). Carbon and hydrogen analyses were performed at the Micro Analytical Services Laboratory of the university of Assiut.

### *Standard procedure*

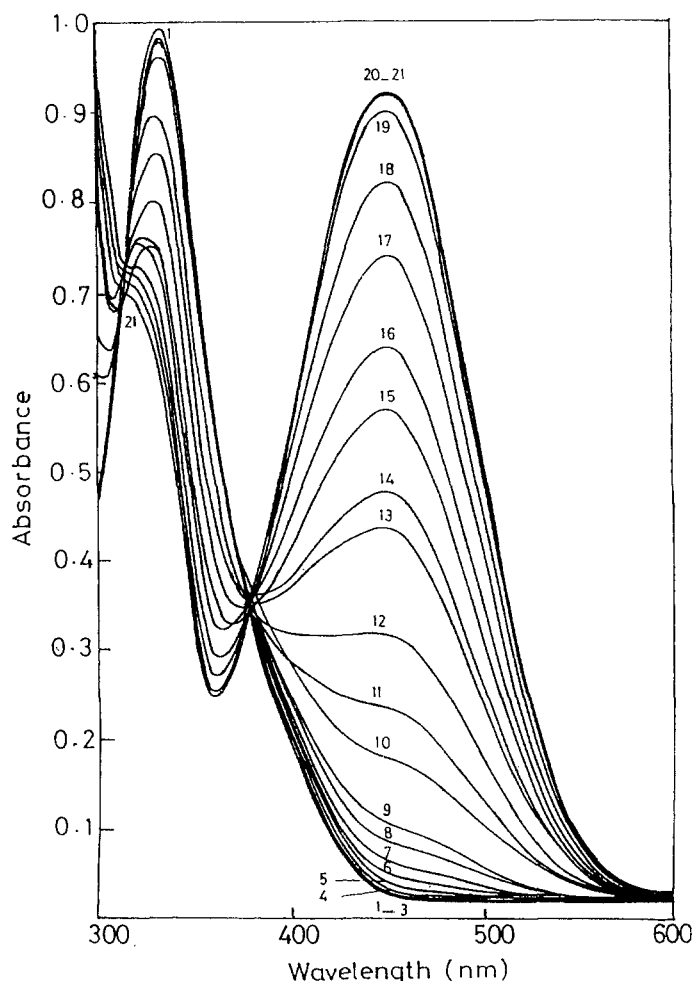
To an aliquot of a solution containing up to 92 µg of zirconium(IV), 5 ml of  $5 \times 10^{-3} M$  *LAS* solution and 2.5 ml of 1 M  $NaClO_4$  solution are added. After mixing with the appropriate amount of

ethanol, the *pH* of the solution is adjusted to 3.3. The mixture is made up to the mark in a 25 ml standard flask with distilled water, and the absorbance is measured at 450 nm against a reagent blank similarly prepared but containing no zirconium(IV).

## Results and Discussion

### *Acid-Base Equilibria of LAS in 40% Ethanol*

The absorption spectra of a  $2 \times 10^{-4} M$  solution of the reagent in 40% ethanol were recorded at various concentrations of  $\text{HClO}_4$  or  $\text{NaOH}$  and at different *pH* values (Fig. 1). The solutions of *LAS* contain three acid-base forms of the reagent, depending on the acidity of the medium ( $\text{LH}_2^+$ ,  $\text{LH}$ , and  $\text{L}^-$ ). The colorless  $\text{LH}_2^+$  species ( $\lambda_{\text{max}} = 330 \text{ nm}$ ), protonated at the free carbonyl oxygen, predominates in solutions of *pH* < 3.5. The molecular yellow form  $\text{LH}$  ( $\lambda_{\text{max}} = 440 \text{ nm}$ ) exists as the prevalent species in the *pH* interval of 3.5–4.8. The orange-yellow mono-anionic form  $\text{L}^-$  ( $\lambda_{\text{max}} = 455 \text{ nm}$ ), dissociated at the hydroxyl group, predominates at *pH* > 5.



**Fig. 1.** Absorption spectra of  $2 \times 10^{-4} M$  *LAS* at different *pH* values in 40% (v/v) ethanol; *pH*: 1) 0.3, 2) 0.5, 3) 1.5, 4) 2.3, 5) 2.65, 6) 2.95, 7) 3.15, 8) 3.45, 9) 3.55, 10) 3.65, 11) 4.0, 12) 4.3, 13) 4.55, 14) 4.6, 15) 4.65, 16) 4.95, 17) 5.05, 18) 5.35, 19) 5.6, 20) 6.0, 21) 6.55

**Table 1.** Values of  $pK_a$  and  $\lambda_{\max}$  for the various forms of *LAS* in 40% (v/v) ethanol

$pK_{ai}$	$\lambda_{\max}(\text{nm})$
$3.58 \pm 0.1(\text{LH}_2^+/\text{LH})$	330 ( $\text{LH}_2^+$ )
$5.45 \pm 0.1(\text{LH}/\text{L}^-)$	440( $\text{LH}$ )
	455( $\text{L}^-$ )

The variation of absorbance with  $pH$  at selected wavelengths was interpreted according to (1) [18], assuming that a particular equilibrium of the form (2) is the only one existing under the specified conditions and characterized by an equilibrium constant  $K_a$ .

$$\log(A - \varepsilon_{\text{LH}_x} c_L) / (\varepsilon_{\text{LH}_{x-1}} c_L - A) = pH - pK_a \quad (1)$$



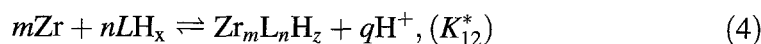
Graphical logarithmic analysis was applied to each wavelength, and the deviation from the mean  $\overline{pK}$  values was evaluated using Eq. (3) where  $\overline{pK}$  is the mean value calculated from  $pK$  values obtained for individual wavelengths  $n$  and  $N_\lambda$  is the number of wavelengths used. The values of  $pK_{a1}(\text{LH}_2^+/\text{LH})$  and  $pK_{a2}(\text{LH}/\text{L}^-)$  are given in Table 1.

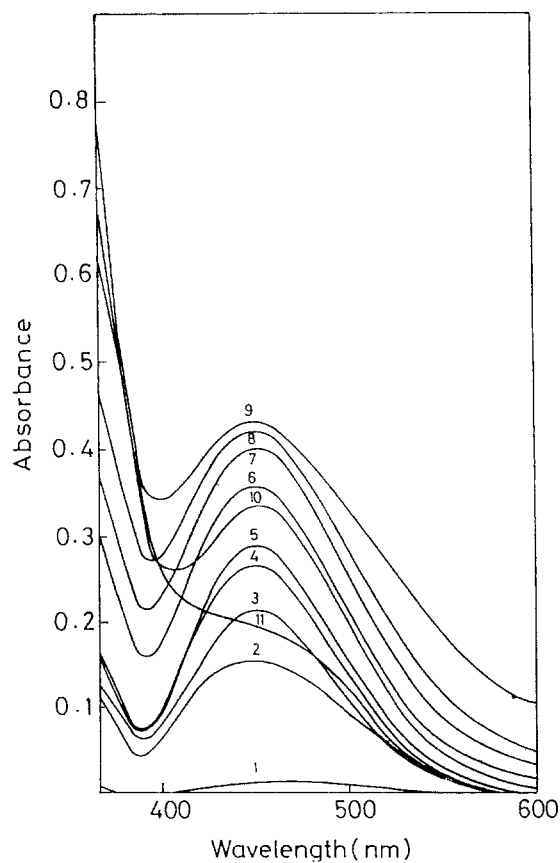
$$\sigma(pK) = \left( \frac{1}{N_\lambda - 1} \sum_{n=1}^{N_\lambda} (\overline{pK} - pK_n)^2 \right)^{1/2} \quad (3)$$

### Complexation Equilibria of Zr(IV) with *LAS*

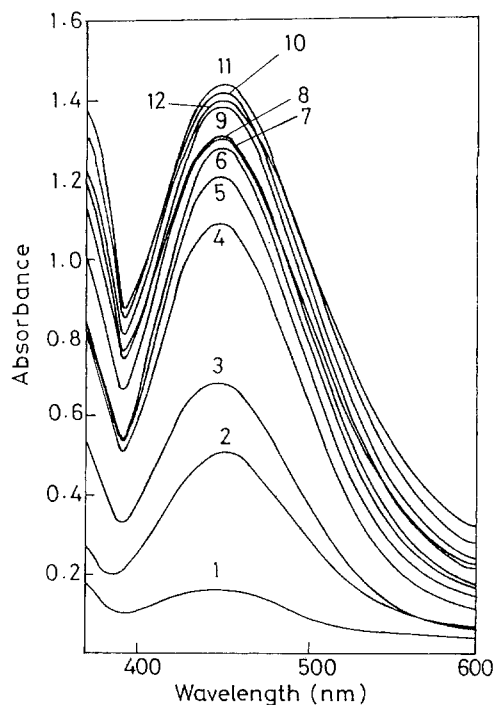
Complex formation of Zr(IV) with *LAS* was investigated at different  $pH$  values in equimolar solutions and solutions containing an excess of one component. The solution spectra indicate the formation of two complexed species in the  $pH$  range of 1.5–3.7, depending on the  $pH$  value of the solution and the concentration of components (Figs. 2 and 3). The absorbance vs.  $pH$  graphs at 450 nm for solutions containing an excess of metal ions indicate the existence of a single chelate equilibrium in the  $pH$  range of 1.5–3.3. For equimolar solutions and solutions with excess of ligand, two inflections in the aforementioned  $pH$  range, can be detected, indicating the existence of two ranges of complex equilibria in solution, probably as a result of a stepwise transition of two complexes (Fig. 4). All absorbance vs.  $pH$  graphs have a similar descending tail above  $pH$  3.7, the shape of which is due to a hydrolysis effect.

Considering the  $pK_a$  values of *LAS*, it can be assumed that the protonated form of the reagent ( $\text{LH}_2^+$ ) is the prevalent ligand species in the range of complexation. The first complexation equilibrium at *ca.*  $pH$  2 probably represents complexation by interaction of Zr(IV) with *LAS* according to Eq. (4).

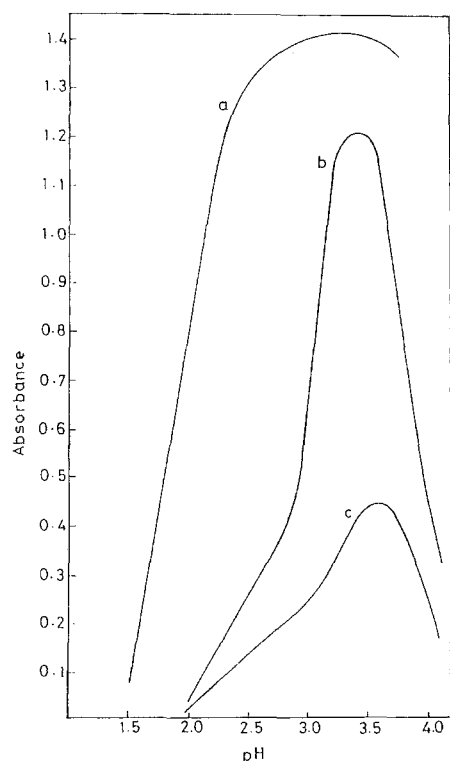




**Fig. 2.** Absorption spectra of Zr(IV)-*LAS* complexes;  $c_M = c_L = 2.5 \times 10^{-4} M$ , 40% (v/v) ethanol; *pH*: 1) 1.7, 2) 1.95, 3) 2.6, 4) 2.8, 5) 3.05, 6) 3.15, 7) 3.25, 8) 3.35, 9) 3.55, 10) 3.65, 11) 3.9

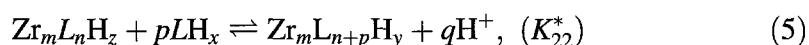


**Fig. 3.** Absorption spectra of Zr(IV)-*LAS* complexes;  $c_M = 6 \times 10^{-4} M$ ,  $c_L = 2 \times 10^{-4} M$ , 40% (v/v) ethanol; *pH*: 1) 1.6, 2) 1.75, 3) 1.9, 4) 2.15, 5) 2.3, 6) 2.45, 7) 2.55, 8) 2.9, 9) 3.1, 10) 3.3, 11) 3.55, 12) 3.8



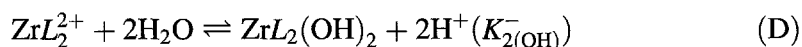
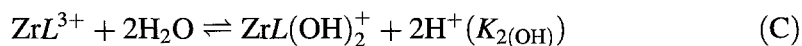
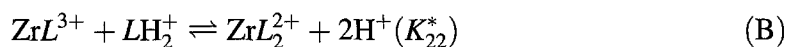
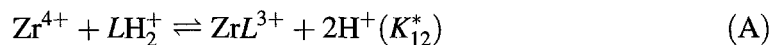
**Fig. 4.** Absorption vs. *pH* graphs for Zr(IV)-LAS complexes at various concentrations of compounds;  $\lambda = 450$  nm,  $I = 0.1$  M (NaClO<sub>4</sub>), 40% (v/v) ethanol; a)  $c_M = 6 \times 10^{-4}$  M,  $c_L = 2 \times 10^{-4}$  M; b)  $c_M = 2.5 \times 10^{-4}$  M,  $c_L = 7.5 \times 10^{-4}$  M, c)  $c_M = c_L = 2.5 \times 10^{-4}$  M

The second complexation equilibrium is attained at *pH* 2.9–3.6 in equimolar solutions and in solutions with excess of ligand, probably as a complex transformation according to Eq. (5).



$K_{12}^*$  and  $K_{22}^*$  are the respective equilibrium constants.

The absorbance vs. *pH* graphs for solutions with an excess of one component or equimolar solutions were interpreted by direct graphical and logarithmic analysis using the relationships reported by *Sommer et al.* [19] and *Idriss et al.* [11] and by a generalized approach described previously [20, 21]. Under the present experimental conditions, one can assume the following equilibria:



The ascending region of the absorbance vs. *pH* graphs in solutions with an excess metal ions in the *pH* range of 1.5–2.8 was analyzed using Eq. (6) assuming equilibrium (4).

$$\log[\Delta A / (\varepsilon_1 c_L - \Delta A)] = qpH + \log c_M + \log K_{12}^* \quad (6)$$

For equimolar solutions, Eq. (7) is valid for equilibrium (4) in the *pH* range of 1.8–2.8.

$$\log[\Delta A/(\varepsilon_1 c_L - \Delta A)^2] = qpH - \log(\varepsilon_1 - \varepsilon_{LH_2^+}) + \log K_{12}^* \quad (7)$$

The logarithmic transformations (6) and (7) are both linear with a slope of  $q = 2$ , indicating the release of two protons during complexation and the formation of a  $ZrL^{3+}$  species according to equilibrium (A). The existence of this complex equilibrium in solutions with excess ligand was proven for the *pH* range of 1.8–2.8 by direct graphical analysis using Eq. (8) and by logarithmic analysis according to Eq. (9).

$$c_M/\Delta A = 1/\varepsilon_1 + [H]^q/K_{12}^* \varepsilon_1 c_L, \quad (8)$$

$$\log[\Delta A/(\varepsilon_1 c_M - \Delta A)] = qpH + \log c_L + \log K_{12}^* \quad (9)$$

The formation of  $ZrL_2^{2+}$  species according to equilibrium (B) was confirmed by analysis of the second ascending branch of the absorbance vs. *pH* graphs in equimolar solutions and solutions with an excess of ligand in the *pH* range of 2.9–3.5 using Eqs. (10) and (11) and considering equilibrium (5) ( $z = 1 + K_{a2}/[H]$ ).

$$c_M/\Delta A = 1/\varepsilon_2 + (\Delta A - \varepsilon_1 c_M)[H]^q Z^p / \Delta A K_{22}^* \varepsilon_2 c_L^p \quad (10)$$

$$\log[(\Delta A - \varepsilon_1 c_M) Z^p / (\varepsilon_2 c_M - \Delta A)] = qpH + p \log c_L + \log K_{22}^* \quad (11)$$

All absorbance vs. *pH* graphs have a descending branch within the *pH* range of 3.6–4.0 which is due to the hydrolysis of the complexed ligand. The graphical and logarithmic analysis of this part of the graphs for solutions with excess metal ions according to equilibrium (C) indicate the hydrolysis of the  $ZrL^{3+}$  species to the hydroxo complex  $ZrL(OH)_2^+$ . For equimolar solutions and solutions with excess ligand, the analysis of the descending branch demonstrates the existence of equilibrium (D).

The equilibrium constants  $K_{12}^*$  and  $K_{22}^*$  are related to the stability constants  $\beta_n$  by the expressions  $\log \beta_1 = \log K_{12}^* + pK_{a2}$  and  $\log \beta_2 = \log \beta_1 + \log K_{22}^* + pK_{a2}$ . The calculated values of molar absorptivities, equilibrium constants, and stability constants of the  $ZrL^{3+}$  and  $ZrL_2^{2+}$  chelates are given in Table 2. The distribution curves for the complex species  $ZrL^{3+}$ ,  $ZrL_2^{2+}$ , and  $ZrL_2(OH)_2$  and for the ligand forms  $LH_2^+$ ,  $LH$ , and  $L^-$  in 40% (v/v) ethanol computed from the overall stability constants of the various complexes or the dissociation constants of the reagent *LAS* are shown in Fig. 5.

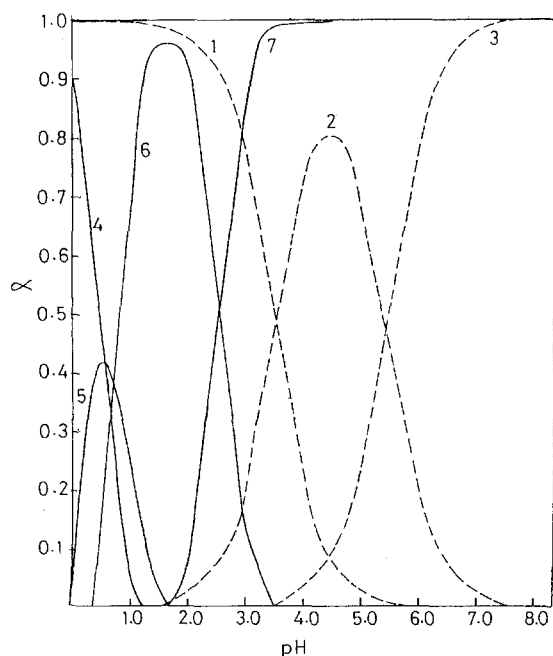
The stoichiometric ratio of the chelates formed was further verified by the method of continuous variation [22]. In solutions with  $c_0 = c_M + c_L = 5 \times 10^{-4} M$  at *pH* = 2.7, the maximum of the *Job* plot corresponds to a component ratio of 1:1 (metal to ligand). At *pH* = 3.3, a component ratio of 1:2 was confirmed.

The solid complex of Zr(IV) with *LAS* with the stoichiometric ratio  $M : L = 1 : 2$  was isolated and characterized. The salient features of the IR spectrum of the solid chelate showed that chelate formation takes place via the carbonyl oxygen and the oxygen of the hydroxyl group and leads to proton elimination. Further, the absence of a new band in the region of 850–950  $cm^{-1}$  due to  $\nu(Zr = O)$  and the appearance of a new band at  $\sim 1145 cm^{-1}$  due to  $\delta(Zr-$

**Table 2.** Mean values of  $\log K^*$ ,  $\log \beta$  and molar absorptivities of Zr(IV)-LAS complexes (averages for various component concentrations,  $I = 0.1 M$  (NaClO<sub>4</sub>), 20°C);

Equilibrium <sup>1</sup>	Constant	log (Constant)	Molar absorptivity ( $l \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ )
$[\text{ZrL}][\text{H}]^2/[\text{Zr}][\text{LH}_2]$	$K_{12}^*$	$(-1.05 \pm 0.02)^2$ $(-1.07 \pm 0.01)^3$ $(-1.09 \pm 0.01)^4$	$5.8 \times 10^3 (\epsilon_1)$
$[\text{ZrL}_2][\text{H}]^2/[\text{ZrL}][\text{LH}_2]$	$K_{22}^*$	$(-1.55 \pm 0.01)^2$ $(-1.68 \pm 0.01)^4$	$1.13 \times 10^4 (\epsilon_2)$
$[\text{ZrL}(\text{OH})_2][\text{H}]^2/[\text{ZrL}]$	$K_{2(\text{OH})}^1$	$(-3.4 \pm 0.02)^3$	
$[\text{ZrL}_2(\text{OH})_2][\text{H}]^2/[\text{ZrL}_2]$	$K_{2(\text{OH})}^1$	$(-5.2 \pm 0.02)^2$ $(-5.6 \pm 0.03)^4$	
$[\text{ZrL}]/[\text{Zr}][\text{L}]$	$\beta_1$	$7.96^5$	
$[\text{ZrL}_2]/[\text{Zr}][\text{L}]^2$	$\beta_2$	$15.30^6$	
$[\text{ZrL}(\text{OH})_2]/[\text{Zr}][\text{L}][\text{OH}]^2$	$\beta_{\text{OH}}$	$32.55^7$	
$[\text{ZrL}_2(\text{OH})_2]/[\text{Zr}][\text{L}]^2[\text{OH}]^2$	$\beta_{2(\text{OH})}^1$	$32.44^8$	

<sup>1</sup> Charges are omitted; <sup>2</sup> from the absorbance vs. *pH* graphs for solutions of equimolar concentration; <sup>3</sup> from the absorbance vs. *pH* graphs for solutions with an excess of metal ion; <sup>4</sup> from the absorbance vs. *pH* graphs for solutions with an excess of ligand; <sup>5</sup> $\beta_1 = K_{12}^*/K_{a1}K_{a2}$ ; <sup>6</sup> $\beta_2 = K_{22}^*\beta_1/K_{a1}K_{a2}$ ; <sup>7</sup> $\beta_{\text{OH}} = K_{2(\text{OH})}B_1/K_{\text{W}}^2$ ; <sup>8</sup> $\beta_{2(\text{OH})}^1 = K_{2(\text{OH})}^1\beta_2K_{a2}/K_{\text{W}}^2$

**Fig. 5.** Distribution curves for the components in the Zr(IV)-LAS system; 40% (v/v) ethanol,  $I = 0.1 M$  (NaClO<sub>4</sub>) curves 1-3:  $c_L = 2 \times 10^{-4} M$ ,  $\alpha = 1$ )  $[\text{LH}_2^+]/c_L$ , 2)  $[\text{LH}]/c_L$ , 3)  $[\text{L}^-]/c_L$ ; curves 4-7:  $c_L = c_M = 2.5 \times 10^{-4} M$ ,  $\alpha = 4$ )  $[\text{Zr}]/c_M$ , 5)  $[\text{ZrL}^{3+}]/c_M$ , 6)  $[\text{ZrL}_2^{2+}]/c_M$ , 7)  $\text{ZrL}_2(\text{OH})_2/c_M$ 

OH) [23] are indicative of the existence of the zirconyl ion as  $\text{Zr}(\text{OH})_2^{2+}$ . The analytical and differential thermal analysis data suggest the formula  $\text{Zr}(\text{OH})_2\text{L}_2 \cdot \text{H}_2\text{O}$  for the 1:2 complex. Experiments to isolate and characterize the 1:1 complex were unsuccessful.



### Calibration Graph and Reproducibility

At the optimum conditions (cf. standard procedure), a linear calibration graph was obtained up to  $4.6 \mu\text{g} \cdot \text{ml}^{-1}$  of Zr(IV). A *Ringbom* plot showed that the optimum range for the determination of Zr(IV) was  $0.92\text{--}3.68 \mu\text{g} \cdot \text{ml}^{-1}$ . The molar absorptivity of the  $\text{Zr}(\text{LAS})_2$  complex at 450 nm was  $1.13 \times 10^4 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ . The sensitivity of the reaction was calculated according to the method of *Sandell* [24] and was found to be  $0.97 \times 10^{-3} \mu\text{g} \cdot \text{cm}^{-2}$  of zirconium. The reproducibility of the method was checked by analyzing two series of ten solutions with zirconium(IV) concentrations of 3.5 and  $1.2 \mu\text{g} \cdot \text{ml}^{-1}$ . The relative standard deviations obtained were found to be 0.8 and 0.55%, respectively.

### Effect of Foreign Ions and Masking Agents

To study the effect of foreign ions upon the determination of Zr(IV), solutions were prepared containing 0.1 mg of Zr(IV) and various concentrations of the ion to be tested. Zirconium(IV) was then determined at optimum conditions. Anions were added as solutions of their sodium or potassium salts, and cations as solutions of their chlorides, nitrates, or acetates. The determination of Zr(IV) as the  $\text{Zr}(\text{LAS})_2$  complex was possible in the presence of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Y}^{3+}$ ,  $\text{Mo}^{6+}$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{S}^{2-}$ ,  $\text{ClO}_4^-$  (20 mg) and  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Mn}^{2+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Ce}^{4+}$ ,  $\text{U}^{6+}$  (8 mg),  $\text{Ti}^{4+}$ ,  $\text{Re}^{3+}$  (2.5 mg). Under the present experimental conditions, Zr(IV) could not be determined in the presence of *EDTA*, fluoride,  $\text{B}_4\text{O}_7^{2-}$ ,  $\text{PO}_3^{3-}$ , or  $\text{S}_2\text{O}_3^{2-}$ .

Accordingly, the above reagents could not be used as masking agents. Interference from the presence of  $\text{Ti}^{4+}$  or large amounts of  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  (12.5 mg) could be eliminated by adding potassium cyanide solution (*ca.* 50-fold excess) as masking agent.

The tolerance criterion for a given ion was taken as the deviation of the absorbance values by more than  $\pm 2\%$  from the value expected for zirconium alone.

**Table 3.** Determination of zirconium in some synthetic samples

Sample composition (%)	Zr(%)		Relative error (%)	Std. dev. (%)
	Added	Found <sup>1</sup>		
Cu: 0.0073; Mg: 8.75; Mn: 0.26; Si: 0.17; Fe: 0.092; Ni: 0.093; Sb: 0.025; Na: 0.13	0.12	0.119	0.83	0.012
C: 0.14; Si: 0.54; S: 0.009; Ti: 0.14; Mn: 0.87; V: 0.36; Nb: 0.034	0.21	0.212	0.95	0.035
Al: 1.54; Ti: 0.33; Fe: 0.042; U: 0.027; Si: 14.85	47.9	48.15	0.52	0.072

<sup>1</sup> mean value for 6 determinations

## Applications

The method has been successfully applied to the direct determination of zirconium in some synthetic samples with compositions similar to those of aluminium alloy, steel, and zircon samples. The results obtained are listed in Table 3.

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