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Complex Equilibria and Spectrophotometric Determination of Mercury(II) with Lawsone

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Summary. The complex equilibria of mercury(II) with Lawsone [2-hydroxy-1,4-naphthoquinone, *LAS*] were studied spectrophotometrically in 40% (*v*/*v*) ethanol water at 20°C and an ionic strength of 0.1 *M* ($NaClO_4$). A complete picture of the solution equilibria in the *pH* range 0.6–4.0 is presented. The complexation reactions were demonstrated and characterized using graphical logarithmic analysis of the absorbance graphs. A simple, rapid, selective, and sensitive method for the spectrophotometric determination of trace amounts of mercury is developed based on the formation of the orange-red $Hg(LAS)_2$ complex at *pH* 2.7. The effect of interferences was studied. The method has been applied to the determination of traces of mercury in different matrices and some organomercury compounds.

Keywords. Mercury(II) determination; Lawsone; Spectrophotometry; Complex equilibria.

Komplex-Gleichgewichte und spektrophotometrische Bestimmung von Quecksilber(II) mit Lawson

Zusammenfassung. Die Komplex-Gleichgewichte von Quecksilber(II) mit Lawson (2-Hydroxy-1,4-naphthochinon, *LAS*) wurden spektrophotometrisch in 40% (*v*/*v*) Ethanol/Wasser bei 20 °C und einer Ionenstärke von 0.1 *M* ($NaClO_4$) untersucht. Es wird ein umfassendes Bild der Gleichgewichte im *pH*-Bereich von 0.6–4.0 gegeben. Die Komplexierungsreaktionen werden mittels graphischer, logarithmischer Analyse der Absorptions-Graphen charakterisiert. Es wird eine einfache, schnelle, selektive und empfindliche Methode für die spektrophotometrische Bestimmung von Quecksilber als Spurenbestandteil mittels der Bildung des orangeroten $Hg(LAS)_2$-Komplexes bei *pH* 2.7 entwickelt. Interferenzen mit anderen Ionen wurden untersucht. Die Methode wurde für die Bestimmung von Quecksilberspuren in verschiedenen Materialien und einigen Organoquecksilberverbindungen verwendet.

Introduction

Many investigations have been made regarding the spectrophotometric determination of mercury(II) [1]. The standard method based on the reaction with dithiozone has been considered unsatisfactory because of its extreme sensitivity to variation in laboratory conditions, while the diphenylcarbazone method has serious drawbacks because of its extreme sensitivity to changes in acidity. Rhodamine B [2], phthalein complexone [3], and xylenol orange [4] were also employed as spectrophotometric reagents for mercury(II). These methods suffer from a number of interferences and are not sufficiently sensitive. Although several other procedures

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** Central Laboratory, Faculty of Science, University of Assiut have been proposed during the past decade for direct, or extraction spectrophotometric determination of mercury(II) [5–12], there is a need for a simple, rapid and sensitive method with a faster colour development which does not require rigid control of *pH*.

In this paper, fundamental studies of the complexation equilibria of Lawsone [2-hydroxy-1,4-naphthoquinone, *LAS*] with Hg(II) in 40% *v*/*v* ethanol is described. The reaction of mercury with this reagent has not yet been investigated. The present work was aimed at establishing the equilibria that exist in solution and at determining the basic characteristics of the complexes formed. The optimum conditions favouring the direct spectrophotometric determination of trace levels of mercury using *LAS* have been investigated.

Experimental Part

Mercury(II) standard solution: A stock solution of $5 \cdot 10^{-3}\,M$ Hg(II) was prepared using AnalaR mercury(II) nitrate in 0.05 *M* nitric acid. The concentration of mercury(II) was determined by *EDTA* titration. 2-hydroxy-1,4-naphthoquinone, Lawsone (*LAS*): Stock solution, $2 \cdot 10^{-3}\,M$ in ethanol. Prepared using Aldrich reagent. Sodium hydroxide standard solution, 0.1 *M*. Ammonium fluoride solution, 0.1 *M*: Prepared using BDH chemicals. Phenylmercury(II) acetate and 4-hydroxymercury(II)benzoate, sodium salt: Obtained from Aldrich products and used as received. Sodium perchlorate and perchloric acid standard solutions and solutions of the foreign ions used for interference studies were prepared from analytical reagent grade chemicals using de-ionised water. Spectrograde ethanol was used. The acidity of the solutions investigated was adjusted by the addition of either dilute perchloric acid or sodium hydroxide. The ionic strength was kept constant at $I = 0.1$ by the addition of sodium perchlorate.

The absorption spectra of solutions were recorded on a Perkin-Elmer Lamda 3B spectrophotometer in the range of 250–600 nm using 1 cm matched quartz cells. Values of *pH* were obtained using a Radiometer *pH* meter (Model M 63) equipped with a Radiometer combined glass electrode (GK 2301 C). The *pH* meter was calibrated regularly with standard buffer solutions. All measurements were performed in the presence of 40% *v*/*v* ethanol and at 20°C. Values of *pH* determined in the partially aqueous solutions were corrected as described elsewhere [13].

Infrared spectra of the reagent and the solid chelate were recorded as CsBr discs on a Perkin-Elmer 599 B IR spectrophotometer. The molar conductivity of the complex was measured using an Industrial Instruments conductance bridge (Model RC-16B2). Carbon and hydrogen analyses were performed at the Micro Analytical Services Laboratory of this department.

Standard Procedure

Into a 25-ml volumetric flask, transfer a suitable aliquot of sample solution containing up to 500 µg of mercury(II), 2 ml of $5 \cdot 10^{-3}\,M$ *LAS* solution and 2.5 ml of 1 *M* $NaClO_4$. After mixing with the appropriate amount of ethanol the *pH* of the solution was adjusted to 2.7 with dilute $HClO_4$. The resulting solution was made up to volume with de-ionized water and the absorbance was measured at 490 nm by using 1 cm quartz cell against a similarly prepared blank of the same *pH*. Under these conditions, the absorbance of the reagent blank at 490 nm measured versus doubly-distilled water was 0.016 ± 0.002 (10 samples).

Results and Discussion

Acid-Base Equilibria of LAS in 40% Ethanol

The absorption spectra of a $10^{-4}\,M$ solution of the reagent in 40% ethanol and at various concentrations of $HClO_4$ or NaOH were recorded as the dependence

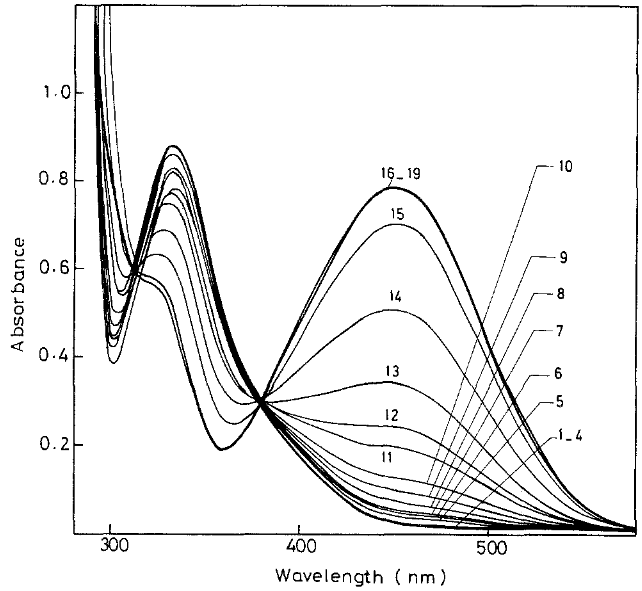

Fig. 1. Absorption spectra of $3 \cdot 10^{-4} M$ *LAS* at different *pH* values in the presence of 40% (*v*/*v*) ethanol. *pH*: *1* 0.6; *2* 1.20; *3* 1.85; *4* 2.05; *5* 2.6; *6* 2.75; *7* 2.9; *8* 3.10; *9* 3.25; *10* 3.45; *11* 3.65; *12* 3.9; *13* 4.45; *14* 5.35; *15* 5.70; *16* 6.5; *17* 7.65; *18* 8.3; *19* 9.2

Table 1. Values of pK_a and λ_{max} for various forms of *LAS* in 40% (*v*/*v*) ethanol; species in parentheses

pK_{a_i}	λ_{max}, nm (main band)
3.58 ± 0.01 (LH_2^+/LH) 5.45 ± 0.02 (LH/L^-)	330 (LH_2^+) 440 (LH) 455 (L^-)

$A = f(\lambda)$ for various *pH* (see Fig. 1). The solutions of *LAS* contains three acid-base forms of the reagent, LH_2^+, LH, and L^- which are dependent on the acidity of the medium. The colorless LH_2^+ species ($\lambda_{max} = 330$ nm) protonated on the free carbonyl oxygen predominates in solutions of $pH < 3$. The molecular yellow form LH ($\lambda_{max} = 440$ nm) exists as the prevalent species in the *pH* interval 3.5–4.8. The orange-yellow monoanionic form L^- ($\lambda_{max} = 455$ nm) dissociated at the hydroxyl group, predominates at $pH > 5$. The absorbance-*pH* graphs at selected wavelengths were interpreted according to the relation [14]

$$\log(A - \varepsilon_{LH_x} C_L)/(\varepsilon_{LH_{x-1}} C_L - A) = pH - pK_a, \tag{1}$$

assuming that a particular equilibrium of the form

$$LH_x \rightleftharpoons LH_{x-1} + H^+, K_a \tag{2}$$

is the only existing under the specified conditions.

Graphical logarithmic analysis was applied to each wavelength and the deviation from the mean $\overline{pK}$ values was evaluated using the equation

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

where $\overline{pK}$ is the mean value calculated from pK values obtained from curves for an individual wavelength n and N_λ is the number of wavelengths used. The values of pK_{a_1} ($L\text{H}_2^+/L\text{H}$) and pK_{a_2} ($L\text{H}/L^-$) are given in Table 1.

Complexation Equilibria of Hg(II) *with LAS*

Complex formation of Hg(II) with *LAS* was investigated at different *pH* values in equimolar solutions and in solutions containing an excess of one component. The solution spectra reflect the formation of at least two complex species in the *pH* range 0.6–3.2 depending on the *pH* of the reaction mixture and the concentration of components (Figs. 2–4). The absorbance-*pH* graphs for solutions containing an excess of metal ions or equimolar solutions at 455 and 495 nm are analogous and indicate the existence of a single chelate equilibrium in the *pH* range 0.6–1.8, probably through interaction of Hg(II) with the $L\text{H}_2^+$ form of the ligand *LAS* according to the general equilibrium

$$m\text{Hg} + nL\text{H}_x \overset{*K_1}{\rightleftharpoons} \text{Hg}_m L_n \text{H}_z + q\text{H}^+ . \tag{4}$$

The graphs in both cases show a decrease of absorbance within the *pH* range 1.9–2.4, followed by a flat part up to *pH* ~ 3.2 which denotes a complex transition of the type

$$\text{Hg}_m L_n \text{H}_z \overset{K_{kal}}{\rightleftharpoons} \text{Hg}_m L_n \text{H}_{z-q} + q\text{H}^+ . \tag{5}$$

Above *pH* ~ 3.4, the absorbance decreases rapidly owing to the hydrolysis of the complexe ligand. In the presence of excess metal ions, the hydrolysis begins to take place at *pH* 2.9.

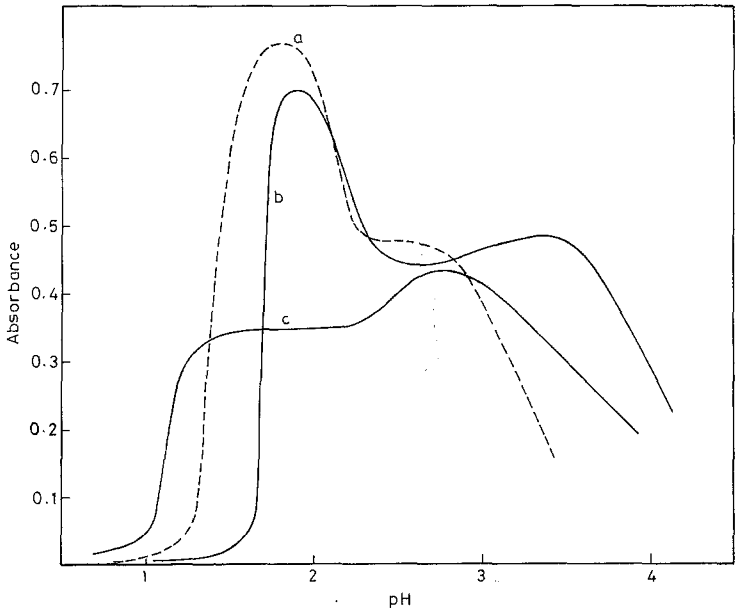

Fig. 2. Absorbance vs. *pH* graphs for Hg(II)-*LAS* systems of various concentrations of components (*a*) $C_L = 1 \cdot 10^{-4} M$, $C_M = 3 \cdot 10^{-4} M$; (*b*) $C_L = C_M = 1 \cdot 10^{-4} M$ and (*c*) $C_L = 3.5 \cdot 10^{-4} M$; $C_M = 0.5 \cdot 10^{-4} M$. $\lambda = 495$ nm, $I = 0.1$ in the presence of 40% (*v*/*v*) ethanol

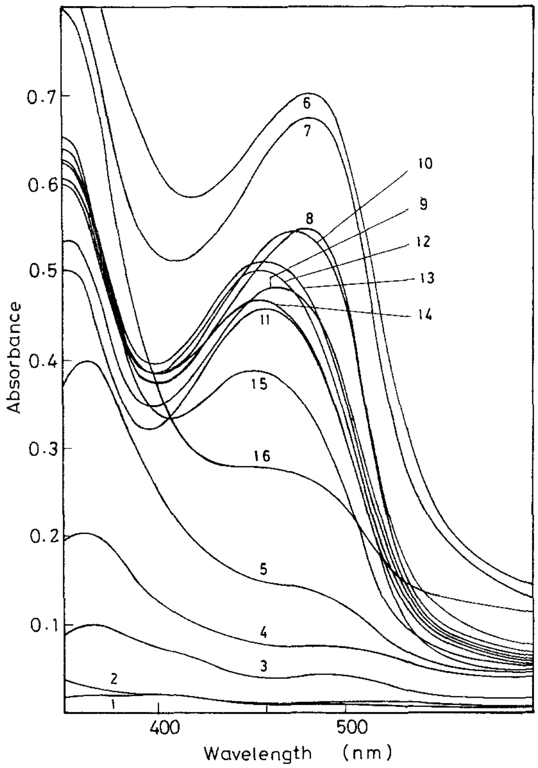

Fig. 3. Absorption spectra of Hg(II)-*LAS* complexes, $C_L = C_M = 1 \cdot 10^{-4} M$. 40% ethanol, *pH*: *1* 1.05; *2* 1.32; *3* 1.60; *4* 1.65; *5* 1.70; *6* 1.85; *7* 2.10; *8* 2.22; *9* 2.37; *10* 2.47; *11* 2.65; *12* 2.97; *13* 3.15; *14* 3.60; *15* 3.78; *16* 4.05

The absorbance-*pH* graphs for solutions containing excess ligand (see Fig. 2) indicated the existence of two basic equilibria within the *pH* range 0.6–2.9 that are sufficiently separated. In addition to equilibrium (4), the second ascending portion of these graphs is attained in the *pH* region 2.2–2.8, probably as a stepwise complex transition with further ligand species coordinated

$$\mathrm{Hg}_m L_n \mathrm{H}_z + pL\mathrm{H}_x \overset{*K_2\,(q\mathrm{H})}{\rightleftharpoons} \mathrm{Hg}_m L_{n+p} \mathrm{H}_c + q\mathrm{H}^+ . \tag{6}$$

The graphs have also a descending branch above *pH* 3 due to the hydrolysis of the complex.

The absorbance-*pH* graphs for solutions with an excess of one component or equimolar solutions were interpreted by direct graphical and logarithmic analysis using the earlier derived slope-intercept transformations of the equilibrium constants of the assumed complex for conditions under which a single equilibrium predominates and for selected wavelength [15].

By considering values of the dissociation constants of *LAS* under our experimental conditions, it can be concluded that the cationic form ($L\mathrm{H}_2^+$) is the prevalent ligand species in the *pH* range of complexation.

The following equilibria were considered during direct and logarithmic analysis of the absorbance-*pH* graphs:

$$\mathrm{Hg}^{2+} + L\mathrm{H}_2^+ \overset{*K_{11}}{\rightleftharpoons} \mathrm{Hg}L\mathrm{H}^{2+}\,(\varepsilon_{1\mathrm{H}}) + \mathrm{H}^+ , \tag{A}$$

$$\mathrm{Hg}^{2+} + L\mathrm{H}_2^+ \overset{*K_{12}}{\rightleftharpoons} \mathrm{Hg}L^+\,(\varepsilon_1) + 2\,\mathrm{H}^+ , \tag{B}$$

$$\mathrm{Hg}L\mathrm{H}^{2+} \quad \overset{*K_{kal}}{\rightleftharpoons} \quad \mathrm{Hg}L^{+}(\varepsilon_1) + \mathrm{H}^{+}\,, \tag{C}$$

$$\mathrm{Hg}L^{+} + L\mathrm{H}_2^{+} \quad \overset{*K_{22}}{\rightleftharpoons} \quad \mathrm{Hg}L_2(\varepsilon_2) + 2\,\mathrm{H}^{+}\,, \tag{D}$$

$$\mathrm{Hg}L^{+} + 2\,\mathrm{H_2O} \quad \overset{*k(2\,\mathrm{OH})}{\rightleftharpoons} \quad \mathrm{Hg}L(\mathrm{OH})_2^{-} + 2\,\mathrm{H}^{+}\,, \tag{E}$$

$$\mathrm{Hg}L_2 + 2\,\mathrm{H_2O} \quad \overset{k'(2\,\mathrm{OH})}{\rightleftharpoons} \quad \mathrm{Hg}L(\mathrm{OH})_2^{-} + L\mathrm{H} + \mathrm{H}^{+}\,. \tag{F}$$

The ascending region of the absorbance-*pH* graphs in solutions with excess metal ions in the *pH* range 1.1–1.8 was analysed using Eq. (7) and assuming equilibrium (4) with $n = m = 1$,

$$\log\left[\Delta A/(\varepsilon_1 C_L - \Delta A)\right] = q\,pH + \log C_M + \log{}^{*}K_{11}\,. \tag{7}$$

For equimolar solutions, Eq. (8) is valid for equilibrium (4) in the *pH* range 1.4–1.9,

$$\log\left[\Delta A/(\varepsilon_1 C_L - \Delta A)^2\right] = q\,pH - \log(\varepsilon_1 - \varepsilon_{L\mathrm{H}_2^+}) + \log{}^{*}K_{11}\,. \tag{8}$$

The logarithmic transformations (7) and (8) are both linear with a slope $q = 1$, indicating the release of one proton during complexation and the formation of a $\mathrm{Hg}L\mathrm{H}^{2+}$ species according to equilibrium (A). The existence of this complex equilibrium is not proved in solutions with excess ligand in the *pH* range 0.8–1.4 as evidenced by the analysis of the initially rising region of the absorbance-*pH* graphs. Direct graphical analysis using Eq. (9) and logarithmic analysis according to Eq. (10) indicated the splitting of two protons and the formation of the $\mathrm{Hg}L^{+}$ complex species according to equilibrium (B),

$$C_M/\Delta A = 1/\varepsilon_1 + [\mathrm{H}]^q/{}^{*}K_{12}\,\varepsilon_1 C_L\,, \tag{9}$$

$$\log\left[\Delta A/(\varepsilon_1 C_M - \Delta A)\right] = q\,pH + \log C_L + \log{}^{*}K_{12}\,. \tag{10}$$

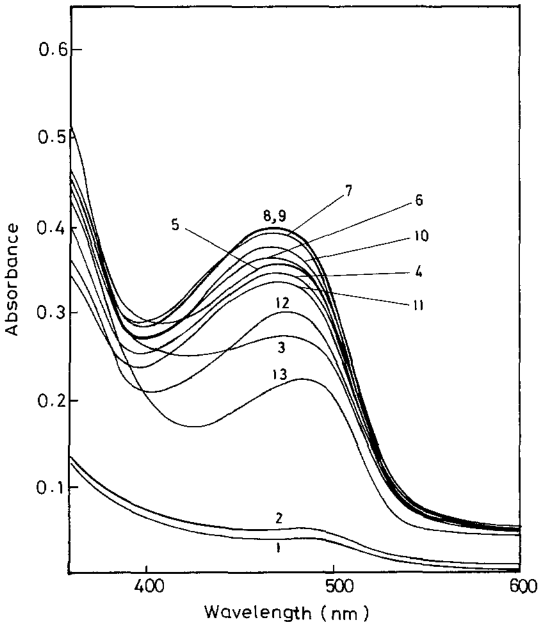

Fig. 4. Absorption spectra of Hg(II)-*LAS* complexes, $C_L = 3.5 \cdot 10^{-4}\,M$, $C_M = 5 \cdot 10^{-5}\,M$, 40% ethanol, *pH*: *1* 0.85, *2* 1.05; *3* 1.15; *4* 1.50; *5* 1.70; *6* 2.25; *7* 2.40; *8* 2.60; *9* 2.85; *10* 3.12; *11* 3.40; *12* 3.60; *13* 4.10

Table 2. Mean values of equilibrium ($\log K^*$) stability constants ($\log \beta$) and molar absorptivities of mercury(II)-*LAS* complexes. Values are taken as averages for various component concentrations, $I = 0.1\,M$ ($NaClO_4$), 20°C

Equilibrium()	Constant	log constant	Molar absorptivity $1\,mol^{-1}\,cm^{-1}$
$[HgLH][H]/[Hg][LH_2]$	$^*K_{11}$	(1.26 ± 0.02)[a], (1.15 ± 0.03)[b]	(ε_{1H}) 7 543
$[HgL][H]/[HgLH]$	$^*K_{kal}$	(-1.5 ± 0.01)[a], (-1.45 ± 0.02)[b]	(ε_1) 5 260
$[HgL][H]^2/[Hg][LH_2]$	$^*K_{12}$	(-0.28 ± 0.01)[c]	(ε_1) 5 075
$[HgL_2][H]^2/[HgL][LH_2]$	$^*K_{22}$	(-1.09 ± 0.02)[c]	(ε_2) 8 920
$[HgL(OH)_2][H]^2/[HgL]$	$k_{(2OH)}$	(-4.4 ± 0.03)[a], (-4.2 ± 0.02)[b]	
$[HgL(OH)_2][LH][H]/[HgL_2]$	$k'_{(2OH)}$	$(-6.6 + 0.01)$[c]	
$[HgLH]/[Hg][HL]$	β_{1H}	4.805[d]	
$[HgL]/[Hg][L]$	β_1	8.77[e]	
$[HgL_2]/[Hg][L]^2$	β_2	16.75[f]	
$[HgL(OH)_2]/[Hg][L][OH]^2$	β_{OH}	32.37[g]	

() Charges are omitted

[a] From the absorbance vs. *pH* graphs for solutions of equimolar concentrations

[b] From the absorbance vs. *pH* graphs for solutions with excess of metal ion

[c] From the absorbance vs. *pH* graphs for solutions with excess ligand

[d] $\beta_{1H} = {}^*K_{11}/K_{a1}$

[e] $\beta_1 = \beta_{1H} \cdot {}^*K_{kal}/K_{a2} = {}^*K_{12}/K_{a1} \cdot K_{a2}$

[f] $\beta_2 = {}^*K_{22} \cdot \beta_1/K_{a1} \cdot K_{a2}$

[g] $\beta_{OH} = k\,(2\,OH) \cdot \beta_1/K_w^2 = k'\,(2\,OH) \cdot \beta_2 \cdot K_{a2}/K_w^2$

The absorbance-*pH* graphs of solutions containing an excess of metal ions or equimolar solutions indicate unambiguously the deprotonation of the $HgLH^{2+}$ complex and exhibit a flat part in the *pH* range 2.4–3. In the *pH* region 1.8–2.3 transformation (11) is linear for deprotonation of the $HgLH^{2+}$ chelate (equilibrium C) and the slope (q) of the logarithmic transformation (12) is unity,

$$C_L/\Delta A = 1/\varepsilon_1 + (\Delta A - \varepsilon_{1H}\,C_L)\,[H]^q/\Delta A\,\varepsilon_1\,K_{kal}, \qquad (11)$$

$$\log\,[(\Delta A - \varepsilon_{1H}\,C_L)\,(\varepsilon_1\,C_L - \Delta A)] = q\,pH + \log K_{kal}, \qquad (12)$$

where K_{kal} is the deprotonation constant of the $HgLH^{2+}$ complex.

The formation of the HgL_2 complex according to equilibrium (D) was confirmed by analysis of the second ascending branch of the absorbance-*pH* graphs in solutions with excess of ligand in the *pH* range 2.2–2.8 using Eqs. (13) and (14) and considering Eq. (6),

$$C_M/\Delta A = 1/\varepsilon_2 + (\Delta A - \varepsilon_1\,C_M)\,[H]^q\,Z^p/\Delta A\,{}^*K_{22}\,\varepsilon_2\,C_L^p, \qquad (13)$$

$$\log\,[(\Delta A - \varepsilon_1\,C_M)\,Z^p/(\varepsilon_2\,C_M - \Delta A)] = q\,pH + p\log C_L + \log {}^*K_{22}, \qquad (14)$$

where $Z = 1 + K_{a2}/[H]$.

All the absorbance-*pH* graphs at various wavelength and concentrations of components have a descending branch within the *pH* range 3–4 which is due to

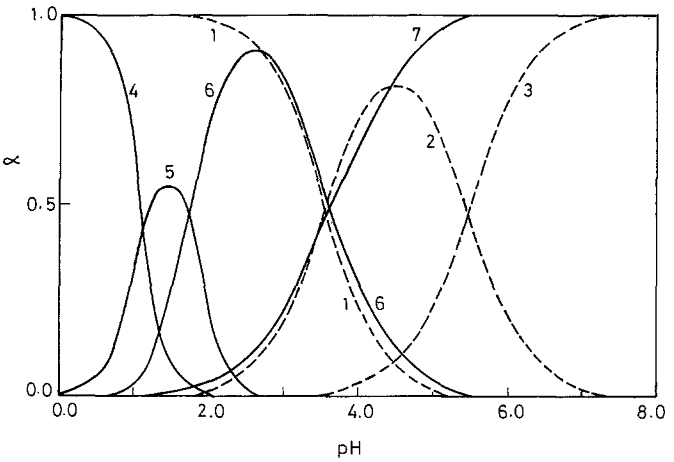

Fig. 5. Distribution curves for the components in the Hg(II)-*LAS* system in 40% (*v*/*v*) ethanol. Curves *1–3* = $C_L = 3 \cdot 10^{-4}\,M$; α = *1)* $[LH_2^+]/C_L$, *2)* $[LH]/C_L$, *3)* $[L^-]/C_L$. Curves *4–7* = $C_L = 3.5 \cdot 10^{-4}\,M$, $C_M = 5 \cdot 10^{-5}\,M$. α = *4)* $[Hg]/C_M$, *5)* $[HgL^+]/C_M$, *6)* $[HgL_2]/C_M$, *7)* $[HgL(OH)_2]/C_M$, $I = 0.1$

the hydrolysis of the complexed ligand. The graphical and logarithmic analysis of this part of the absorbance-*pH* graphs for solutions with excess metal ions according to equilibrium (E) indicate unambiguously the hydrolysis of the HgL^+ complex to the hydroxocomplex $HgL(OH)_2^-$. The existence of this complex transition is also confirmed in equimolar solutions above *pH* 3.4. For solutions with excess ligand, the analysis of the descending branch of the absorbance *pH* graphs at *pH* 3–4 demonstrates the existence of equilibrium (F).

The calculated values of equilibrium ($\log {}^*K$), stability constants ($\log \beta$) and molar absorptivities of Hg(II)-*LAS* complexes are given in Table 2.

The distribution curves for the complex species: HgL, HgL_2 and $HgL(OH_2^-$ and 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 stoichiometry of the chelates formed was further verified by the method of continuous variation [16]. In solutions having $C_0 = C_M + C_L = 3 \cdot 10^{-4}\,M$ at *pH* 1.8, the maximum of the Job plot corresponds to component ratio of 1 : 1 (metal to ligand). At *pH* 2.7, a component ratio of 1 : 2 was confirmed.

The solid complex of Hg(II) with *LAS* with the stoichiometric ratio 1 : 2 (metal : ligand) was isolated and characterised. The salient features of the IR spectrum of the solid chelate showed unambiguously that chelate formation takes place via the carbonyl oxygen and the oxygen of the hydroxyl group and leads to proton elimination. The formulation of the complex as HgL_2 (LH symbolising the neutral form of the reagent) was confirmed by elemental analysis and conductivity measurement. The molar electrical conductance, Λ_m, of reagent grade *DMF* solution of the complex at a concentration of $10^{-3}\,M$ showed that the complex is essentially nonelectrolyte.

Calibration Graph and Reproducibility

At the optimum conditions given under Standard Procedure, a linear calibration graph was obtained up to 20.0 μg ml^{-1} of Hg^{II}. A Ringbom plot showed that the optimum range for the determination of Hg^{II} was 2.3–17.5 $\mu g\,ml^{-1}$. The molar absorptivity of the $Hg(LAS)_2$ complex at 490 nm was $0.89 \cdot 10^4\,l\,mol^{-1}\,cm^{-1}$. The sensitivity of the reaction was calculated according to the method of Sandell [1] and was found to be $4.6 \cdot 10^{-3}\,\mu g\,cm^{-2}$ of mercury. The reproducibility of the method was checked by analysing two series of ten solutions having mercury(II) concentrations of 5 and 12.5 $\mu g\,ml^{-1}$. The relative standard deviations obtained were found to be 0.8 and 0.55%, respectively.

Effect of Foreign Ions and Masking Agents

The effect of foreign ions on the determination of mercury with *LAS* was studied by adding a known quantity of the desired ion to a solution containing 0.4 mg of mercury which was determined by following the procedure described above. Anions were added as solutions of their sodium or potassium salts and cations were added as solutions of their nitrates, perchlorates or sulphates. The determination of Hg(II) as $Hg(LAS)_2$ was possible in the presence of Li^+, Na^+, K^+, Cs^+, Ca^{2+}, Sr^{2+}, Mg^{2+}, NH_4^+, Cd^{2+}, Zn^{2+}, Al^{3+}, SO_4^{2-}, SO_3^{2-}, ClO_4^- (25 mg), Br^-, I^-, Ce^{4+}, U^{6+} (5 mg) and Ag^+ (2 mg). Using the present experimental conditions, it was observed that mercury(II) could be determined in the presence of appreciable amounts of fluoride ions. Interference from large amounts of Ag^+ (up to 20 mg) could be eliminated by adding ammonium fluoride solution (ca. 100-fold-excess) as a masking agent. Samples containing ~ 8 mg of Fe^{3+}, Ba^{2+}, Pb^{2+}, La^{3+} were also easily tolerated in the presence of 100-fold excess of fluoride ions. Interference from Cu^{2+} (up to 5 mg) could be prevented by adding 5-sulphosalicylic acid (~ 20-fold excess) as masking agent. The tolerance criterion for a given ion was taken as the deviation of the absorbance value by more than 2% from the value expected for mercury(II) alone. Of the anions investigated cyanide ions showed serious interference, even when present in amounts of ca. 0.8 mg.

Application of the Method

The standard procedure for the determination of mercury(II) was applied to samples of some organomercurials with an appropriate mercury content after digestion of the organic compound. The recovery of the analysis of phenylmercury(II) acetate (*PMA*) and 4-hydroxymercury(II) benzoate (*HMB*) after digestion with 1 : 1 (*v*/*v*) $HClO_4 : HNO_3$, is given in Table 3.

The procedure was also applied to determination of Hg(II) in five synthetic samples, prepared from analytical grade reagents and including cations that could

Table 3. Determination of mercury(II) in organic materials

Compound	Taken, $\mu g\,ml^{-1}$	Found, $\mu g\,ml^{-1}$	Recovery %
PMA	8	7.72	96.5
	12	11.69	97.4
HMB	15	14.72	98.1

Table 4. Results for Hg(II) in synthetic samples

Sample	Sample composition, %													Hg found (%)	Std. dev. (%)
	Zn	Pb	Mg	Ca	Al	Fe^{3+}	Ba	Cd	Th	Cu	Ag	Mn	Hg		
1	27.60	2.18	7.16	4.21	56.85								1.99	2.07	0.08
2	23.12			14.12				36.48				21.18	5.10	1.91	0.04
3				25.70	43.37					10.21	17.31		3.41	3.47	0.06
4	59.35			14.56		2.54	4.99		16.85				1.71	1.75	0.04
5		9.77	32.07	23.60				28.40					0.50	0.52	0.02

be present in different mineral matrices with mercury. Table 4 shows the composition of samples and the results obtained.

The validity of the proposed method for the determination of mercury in sphalirites was examined. The results obtained for two samples (0.069 and 0.0646% mercury) were in good agreement with those obtained by atomic absorption spectrometry (0.068 and 0.064% mercury, respectively).

Conclusion

LAS reacts selectively with mercury(II) under the optimum conditions and in the presence of ammonium fluoride solution. Aspects of the complex equilibria have been investigated. The reagent offer clear advantages over many of the other chromogenic reagents used for the same purpose. The proposed method has the advantages of simplicity, sensitivity and selectivity. Another advantage of the given procedure are the low absorbance of the reagent blank and high stability of the reagent stock solution.

Symbols Used

C_L	Total concentration of the ligand.
C_M	Total concentration of the metal ion.
$\Delta A = A - A_L$	Differences in the overall absorbance and the absorbance of the reagent blank under the same conditions.
ε_{LH_x} and $\varepsilon_{LH_{x-1}}$	Molar absorptivities of the LH_x and LH_{x-1} species of the reagent.
ε_{1H}, ε_1 and ε_2	Molar absorptivities of $HgLH^{2+}$, HgL^+ and HgL_2 complexes.
q	Number of protons released during complexation.
$^*K_{11}$, $^*K_{12}$, $^*K_{kal}$, $^*K_{22}$, k and k'	Equilibrium constants according to reactions: A, B, C, D, E, and F, respectively.
K_{a1}	Proton dissociation constant (LH_2^+/LH) of the reagent.
K_{a2}	Proton dissociation constant (LH/L^-) of the reagent.
$Z = 1 + K_{a2}/[H]$.	

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