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Studies on the Mixed-Ligand Complexes of Copper(II) with Gallic Acid and Pyridine Carboxylic Acids and their Benzologues

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Summary. The ternary complex formation of copper(II) with gallic acid (*gal*) and 2-hydroxy nicotinic acid (*hyna*), 2-mercapto nicotinic acid (*mena*), salicylic acid (*sa*) or thiosalicylic acid (*tsa*) as a second ligand in a 1:1:1 molar ratio has been investigated in 40% (v/v) ethanol using spectrophotometric and *pH* titration methods. The solution equilibria of the ternary systems have been determined and the stability constants of the mixed complexes has been evaluated. Considering all parameters, the Cu-*gal*-*sa* ternary system was proved as a suitable, rapid, and sensitive spectrophotometric indicator for determining traces of copper.

The ternary system containing *sa* obeys *Beer*'s law up to 3.4 $\mu g \cdot ml^{-1}$ copper. The optimum range for the determination of copper (*Ringbom*) at *pH* 6.0 ranges from 0.63 to 1.74 $\mu g \cdot ml^{-1}$ of copper. The molar absorptivity of the ternary complex is $1.3 \times 10^4 \, l \cdot mol^{-1} \cdot cm^{-1}$.

Keywords. Copper(II) mixed ligand complexes; Gallic acid; Pyridine carboxylic acid; Complexation equilibria; Spectrophotometry; Potentiometry; Determination of copper.

Untersuchungen an *mixed-ligand*–Komplexen von Kupfer(II) mit 3,4,5-Trihydroxybenzoesäure und Pyridincarbonsäuren und ihren C-Homologen

Zusammenfassung. Die Bildung ternärer Komplexe von Kupfer(II) mit 3,4,5-Trihydroxybenzoesäure (*gal*) und 2-Hydroxynicotinsäure (*hyna*), 2-Mercaptonicotinsäure (*mena*), Salicylsäure (*sa*) oder Thiosalicylsäure (*tsa*) in einem molaren Verhältnis von 1:1:1 wurde mittels spektrophotometrischer und potentiometrischer Methoden in 40% (v/v) Ethanol untersucht. Die Lösungsgleichgewichte der termären Systeme und die Stabilitätskonstanten der gemischten Komplexe wurden bestimmt. Unter Berücksichtigung aller Parameter erwies sich das termäre System Cu-*gal*-*sa* als geeigneter schneller und empfindlicher Indikator zur Spurenanalyse von Kupfer.

Das *sa* enthaltende ternäre System gehorcht dem *Beer*schen Gesetz bis zu einer Kupferkonzentration von 3.4 $\mu g \cdot ml^{-1}$. Der optimale Bereich zur Bestimmung von Kupfer (*Ringbom*) bei *pH* 6.0 erstreckt sich von 0.63 bis 1.74 μg Cu pro ml. Die molare Extinktion des ternären Komplexes beträgt $1.3 \times 10^4 \, l \cdot mol \cdot cm^{-1}$.

Introduction

Aromatic hydroxycarboxylic acids are of considerable importance due to their complex formation ability with different metal ions [1, 2]. Although several studies have been made on the use of hydroxybenzoic acids in ternary complex formation

[3, 4], mixed complexes containing gallic acid (3,4,5-trihydroxybenzoic acid, *gal*) as a primary ligand are still scarce. No systematic studies have yet been reported on the complexation reaction of transition metals with gallic acid in presence of hydroxy or mercapto derivatives of pyridinecarboxylic acids. Thus, it seemed of interest to investigate the solution equilibria and stability of the complexes of copper(II) with such *bi*-ligand systems.

The present study was undertaken to investigate the complexation reaction of Cu(II) with gallic acid as a primary ligand and 2-hydroxynicotinic acid, 2-mercaptonicotinic acid, and the benzologuous salicylic and thiosalicylic acids as secondary ligands in 40% (v/v) ethanol. The work was aimed to establish the equilibria that exist in solution and to determine the basic characteristics of the complexes formed. Optimum conditions for the spectrophotometric determination of copper as the Cu-*gal-sa* ternary complex have been determined.

Results and Discussion

Acid-Base Equilibria of Gallic Acid. In 40% (v/v) ethanol–water and in the *pH* range 2–11.5, the ligand *gal* exists in four different forms: neutral ($gal\text{-}H_4$), monoanionic $(gal\text{-}H_3)^-$, dianionic $(gal\text{-}H_2)^{2-}$, and trianionic $(gal\text{-}H)^{3-}$. The absorbance *vs. pH* curves at $\lambda = 630$ and 270 nm show the various ranges of formation and the equilibria in solution in the *pH* range of study. The results obtained proved that the predominant form of *gal* in acidic medium ($pH \leqslant 6.2$) is monoanionic $(gal\text{-}H_3)^-$. The elimination of the proton from the last hydroxyl group seems to be very difficult to perform.

Solution Spectra of Binary and Ternary Complexes. The spectra of *gal* exhibit a main absorption band at $\lambda = 270$ nm within the *pH* range 4.0–6.5, whereas the solution

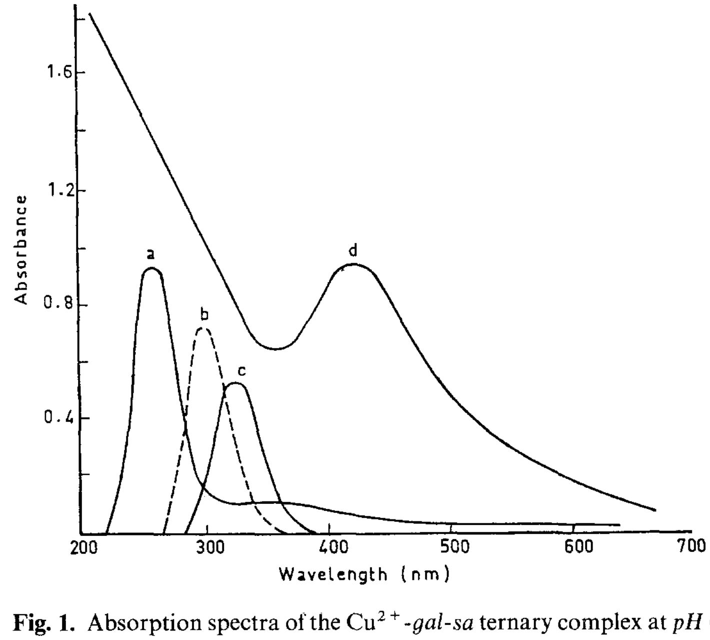

Fig. 1. Absorption spectra of the Cu^{2+}-*gal-sa* ternary complex at *pH* 6.0 (40% (v/v) ethanol, $I = 0.1\ M$ KNO_3). a) *gal*; b) 1:1 Cu^{2+}-*gal vs. gal*; c) 1:1 Cu^{2+}-*sa vs. sa*; d) 1:1:1 Cu-*gal-sa vs. gal-sa*

spectra of the 1:1 Cu^{2+}-*gal* binary complex are characterized by an absorption band with λ_{max} near 300 nm. The spectra of equimolar solutions of Cu^{2+}-*hyna* and Cu^{2+}-*mena* systems exhibit absorption bands at 315 and 305 nm at *pH* 5.7 and 6.2, respectively. The spectra of Cu^{2+}-*sa* or Cu^{2+}-*tsa* complexes are characterized by absorption bands at 320 nm (*pH* 6.0–7.0) and 380 nm (*pH* 7.4–7.8), respectively. However, the spectra of the ternary systems containing equimolar concentrations of Cu^{2+}, *gal*, and the secondary ligand against a reagent blank containing the same concentrations of the two ligands exhibit a new absorption band at 420–430 nm with maximum colour development being attained at *pH* 5.5–7.0 (Fig. 1). The absorbance of solutions of the ternary systems were measured as a function of *pH* at 420 nm.

Complex Equilibria and Stability of the Ternary Complexes. The formation of the ternary complexes was examined at different *pH* values using equimolar concentrations of components. The variation of absorbance values with *pH* at $\lambda = 420$–430 nm (Fig. 2) indicates the existence of two basic equilibria within the *pH* range of study. The absorbance *vs. pH* graphs were analyzed graphically using the relations derived earlier by *Sommer et al.* [7–9]. The analysis of the two rising parts of these graphs was performed assuming the following equations:

$$Cu^{2+} + (gal\text{-}H_3)^- \rightleftharpoons [Cu(gal\text{-}H)]^- + 2\,H^+ \qquad A$$

$$\underset{(\varepsilon_1)}{[Cu(gal\text{-}H)]^-} + HL^- \rightleftharpoons \underset{(\varepsilon_2)}{[Cu(gal\text{-}H)(L)]^{3-}} + H^+ \qquad B$$

Transformation 1 was used for the estimation of the molar absorptivity (ε_2) of the copper ternary complexes.

$$C_M/\Delta A = 1/\varepsilon_2 + (A - \varepsilon_1 C_M)\,[H]^q\, Z/\Delta A\, K^*\, \varepsilon_2 C_L \qquad 1$$

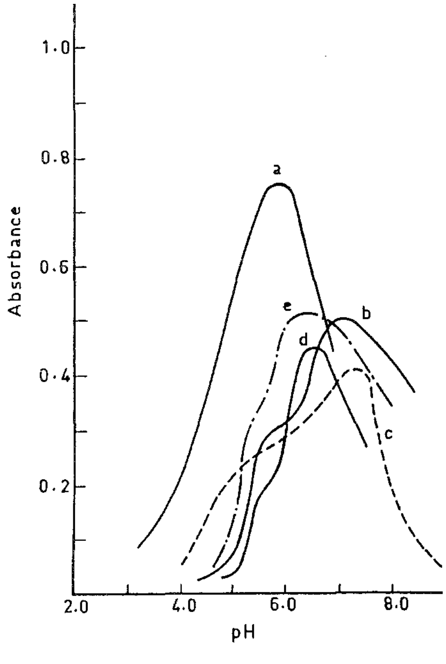

Fig. 2. Absorbance *vs. pH* graphs for binary and ternary systems (40% (v/v) ethanol). a) Cu-*gal* binary system, $C_L = C_M = 5 \times 10^{-4}\,M$, $\lambda = 300$ nm; b) Cu-*gal-hyna* ternary system, $C_L = C_M = 5 \times 10^{-4}\,M$, $\lambda = 430$ nm; c) Cu-*gal-mena* ternary system, $C_L = C_M = 5 \times 10^{-4}\,M$, $\lambda = 425$ nm; d) Cu-*gal-sa* ternary system, $C_L = C_M = 5 \times 10^{-4}\,M$, $\lambda = 420$ nm; e) Cu-*gal-tsa* ternary system, $C_L = C_M = 5 \times 10^{-4}\,M$, $\lambda = 420$ nm

where $Z = 1 + K_{a_2}/[\mathrm{H}]$, and ε_1 and ε_2 are the molar absorptivities of the [Cu (*gal*-H)]$^-$ and [Cu(*gal*-H)]$^{3-}$ complexes, respectively. The transformation was linear assuming the release of one proton ($q = 1$) during the formation of the ternary complex according to equation B. The number of liberated protons (q) as well as the equilibrium constants of reaction B were obtained using equation 2:

$$\log(\Delta A - \varepsilon_1 C_M)Z/(\varepsilon_2 C_M - \Delta A) = q \cdot pH + \log C_L + \log K^* \qquad 2$$

The stability constants of the system Cu-*gal-L* is related to the equilibrium constant K by the equation

$$\log \beta = \log K + \log \beta^{Cu}_{Cu(gal)} + pK_{a_2}(L)$$

The results obtained for the different ternary systems investigated are given in Table 1.

Stoichiometry of the Ternary Complexes. Job's method of continuous variation [10, 11] was applied to find out the composition of the ternary complexes. The results indicate that the overall ratio of the ternary complexes Cu-*gal-hyna, mena, sa,* or *tsa* are 1:1:1. The stoichiometric ratio of the complexes was also confirmed by applying the mole ratio method [12].

Beer's Law, Sensitivity and Precision of the Method. Curves showing the dependence of absorbance on copper concentration based on the ternary complexes with *gal*

Table 1. Mean values of equilibrium constants, stability constants ($\log \beta$) and molar absorptivities (ε) of the ternary copper(II) complexes (Cu-*gal-L*) with gallic acid (*gal*) and secondary ligands (*L*). Values are taken as averages of various component concentration $I = 0.1\ M$ (KNO_3); 25 °C, 40% (v/v) ethanol

Equilibrium[a]	Constant	log(Constant)[b]	Molar absorptivity (ε)Cu-*gal-hyna*
	Cu-*gal-hyna*		
$[M(gal)]/[M][gal]$	$\beta^{Cu}_{Cu(gal)}$	7.79	1×10^4
$[M(gal)(L)][H]/[M\ gal][HL]$	K	2.40	
$[M(gal)(L)]/[M][gal][L]$	β	19.91	
	Cu-*gal-mena*		
$[M(gal)]/[M][gal]$	$\beta^{Cu}_{Cu(gal)}$	7.70	0.6×10^4
$[M(gal)(L)][H]/[M\ gal][HL]$	K	1.10	
$[M(gal)(L)]/[M][gal][L]$	β	17.64	
	Cu-*gal-sa*		
$[M(gal)]/[M][gal]$	$\beta^{Cu}_{Cu(gal)}$	7.53	1.3×10^4
$[M(gal)(L)][H]/[M\ gal][HL]$	K	2.00	
$[M(gal)(L)]/[M][gal][L]$	β	23.39	
	Cu-*gal-tsa*		
$[M(gal)]/[M][gal]$	$\beta^{Cu}_{Cu(gal)}$	7.79	0.82×10^4
$[M(gal)(L)][H]/[M\ gal][HL]$	K	2.20	
$[M(gal)(L)]/[M][gal][L]$	β	19.22	

[a] Charges are omitted; [b] $\log \beta = \log K + \log \beta^{Cu}_{Cu(gal)} + pK_{a_2}(L)$

and one of the investigated secondary ligands (*L*) satisfy *Beer*'s law for copper concentrations up to 7.0 μg·ml^{-1}. The optimum range for accurate determinations as evaluated from *Ringbom* plots and *Sandell*'s sensitivity index [13] for $A = 0.001$ are 1.27–3.81 μg·ml^{-1} Cu and 1.6×10^{-3} μg·cm^{-2} (*hyna*) 1.27–4.5 μg·ml^{-1} Cu and 1.6×10^{-3} μg·cm^{-2} (*sa*), and 0.9–3.3 μg·ml^{-1} Cu and 1.9×10^{-3} μg·cm^{-2} (*tsa*). The reproducibility of the method was checked by testing two series of solutions having copper concentrations of 1.5 and 3.0 μg·ml^{-1}, respectively. The relative standard deviation was found to be less than 1%.

Effect of Diverse Ions. Varying amounts of diverse ions were employed with fixed amounts of copper (0.08 mg) and the recommended procedure was followed. The determination of Cu^{2+} as a ternary complex was possible in the presence of 20 mg of Li^+, Na^+, K^+, Ag^+, Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}, Sn^{2+}, Pb^{2+}, As^{3+}, La^{3+}, Th^{4+}, SO_4^{2-}, NO_3^-, ClO_4^-, $B_4O_7^{2-}$, Cl^-, Br^-, F^-, acetate, and citrate. The determination of Cu^{2+} was also possible in the presence of Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, $H_2PO_4^-$ (7.0 mg) and Al^{3+} (4.0 mg) or Bi^{2+} (1 mg). Under our experimental conditions it was observed that Cu^{2+} could be determined in the presence of appreciable amounts of cyanide or fluoride ions (~50 fold excess). Interference from large amounts of Fe^{3+} (up to 10 mg) could be eliminated by adding ammonium fluoride solution (ca ~50 fold excess) as a 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 Cu^{2+} alone.

Applications of the Method. Based on the results of the four ternary systems described above (Table 1), the Cu-*gal*-*sa* ternary system appears to be the best for the determination of copper. The given procedure is highly selective for the deter-

Table 2. Determination of copper in various samples

Cu taken (μg/25 ml)	Foreign ions added (μg/25 ml)		Cu found (μg/25 ml)
80.0	Mn^{2+}	800	80.00, 79.98
	Al^{3+}	500	
	Ni^{2+}	500	
60.0	Co^{2+}	150	59.70, 60.00
	Sn^{2+}	50	
	Mn^{2+}	50	
	Ni^{2+}	50	
40.0	Zn^{2+}	500	39.96, 40.10
	Pb^{2+}	50	
	Fe^{3+}	50	
Brass*			56.86%, 56.88%
Aluminium alloy*			3.98%, 3.99%

* Reported content (%): Brass, Cu 56.9, Pb 2.35, Zn 40.65, Fe 0.009; Aluminium Alloy, Cu 4.0, Ni 2.12, Mn 1.7, Fe 0.031, rest Al

mination of copper and is sufficiently sensitive for analysis of some synthetic samples as well as a variety of copper containing alloys. The results are accurate and the wide applicability of the method has been demonstrated by the satisfactory analysis of synthetic mixtures and standard samples (Table 2).

pH-Metric Titrations. The dissociation constants $pK^{H}_{(gal\text{-}H_4)}$, $pK^{H}_{(gal\text{-}H_3)^-}$ and $pK^{H}_{(gal\text{-}H_2)^{2-}}$ of gallic acid in 40% (v/v) ethanol–water were determined potentiometrically using the *Irving–Rossotti pH* titration technique [14] with modifications [15, 16]. The details regarding the potentiometric method have been reported earlier [4]. The values of the dissociation constants of *hyna*, *mena*, *sa*, and *tsa* ($pK^{H}_{H_2L}$) were also determined under the same experimental conditions (Table 3). The stability constants of the binary complexes were calculated from titration graphs in which the metal:ligand ratio was 1:3. The values are given in Table 3.

Potentiometric titration curves for ternary systems containing Cu^{2+}-*gal* and *tsa*, *hyna*, or *mena* in a 1:1:1 molar ratio exhibit a single steep inflection at $m = 4$ (m = mole of base added per mole of metal ion). In ternary systems including *sa* as secondary ligand, well defined inflections are obtained at $m = 3$ (Fig. 3). Analysis of these curves indicates that the 1:1:1 (Cu*AL*) ternary complex is formed in all cases. The formation constants for these complexes are listed in Table 3.

Generally, the experimental data show that the formation of the ternary complexes shifts the buffer region of the ligands to lower *pH* values, which indicates that the ternary complexes are more stable than the binary complexes. According to our results, the complex equilibria of the Cu*AL* ternary complexes can be represented by the following schemes:

i) for *tsa*, *hyna* or *mena* as second ligand:

$$Cu^{2+} + (gal\text{-}H_3)^- \rightleftharpoons [Cu(gal\text{-}H)]^- + 2H^+,\ K^{Cu}_{Cu(gal\text{-}H)} \qquad 3$$

$$[Cu(gal\text{-}H)]^- + H_2L \rightleftharpoons [Cu(gal\text{-}H)L]^{3-} + 2H^+,\ K^{Cu(gal\text{-}H)}_{Cu(gal\text{-}H)L} \qquad 4$$

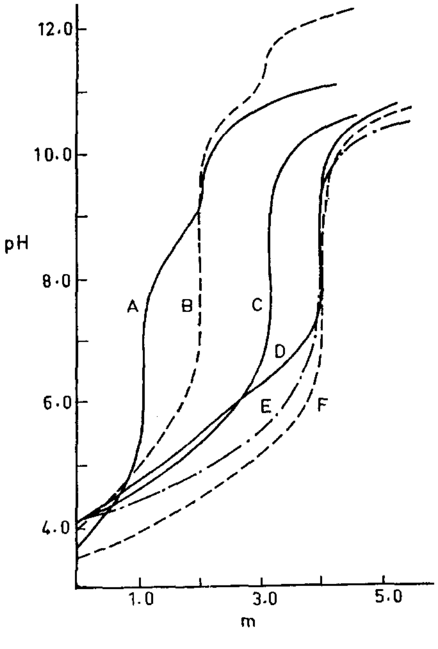

Fig. 3. Potentiometric titration curves for *gal*, 1:1 Cu^{2+}-*gal*, and 1:1:1 Cu^{2+}-*gal*-secondary ligand systems ($I = 0.1\,M$ KNO_3, 40% (v/v) ethanol; m represents the number of moles of base per mole of metal ion; for curve A the abscissa represents the number of moles of base added per mole of ligand). A) *gal*; B) 1:1 Cu^{2+}-*gal*; C) 1:1:1 Cu^{2+}-*gal-sa*; D) 1:1:1 Cu^{2+}-*gal-hyna*; E) 1:1:1 Cu^{2+}-*gal-mena*; F) 1:1:1 Cu^{2+}-*gal-tsa*

Table 3. Acidity constants[a] of the ligands and stability constants of binary and mixed ligand copper(II) complexes[b] and some related data ($I = 0.1\ M$ (KNO_3), 25 °C, 40% (v/v) ethanol)

Ligand (L)	pK	$\log K^{Cu}_{CuL}$	$\log K^{CuL}_{CuL_2}$	$\log \beta^{Cu}_{CuL_2}$	$\log K^{Cu(gal)}_{Cu(gal)L}$	$\log \beta^{Cu}_{Cu(gal)L}$	$\Delta\log K_{Cu}$
gal[d]	10.7 (H/H_2L)	9.98	9.14	19.12	–	–	–
hyna	6.25 (H/H_2L) 9.72 (H/HL)	8.50	7.95	16.45	9.05	19.03	+0.55
mena	5.40 (H/H_2L) 8.84 (H/HL)	7.40	–	–	7.80	17.78	+0.40
sa	3.42 (H/H_2L) 13.86[c] (H/HL)	11.19	10.51	21.70	12.10	22.08	+0.91
tsa	4.35 (H/H_2L) 9.23 (H/HL)	8.14	–	–	8.60	18.58	+0.46

[a] Constants accurate to ±0.02; [b] constants accurate to ±0.05; [c] Ref. [20]; [d] $pK^{H}_{H_4L}(gal) = 4.4$; $pK^{H}_{H_3L} = 8.51$

ii) for *sa* as second ligand:

$$Cu^{2+} + (gal\text{-}H_3)^- \rightleftharpoons [Cu(gal\text{-}H)]^- + 2H^+,\ K^{Cu}_{Cu(gal\text{-}H)} \qquad 5$$

$$[Cu(gal\text{-}H)]^- + HL^- \rightleftharpoons [Cu(gal\text{-}H)L]^{3-} + H^+,\ K^{Cu(gal\text{-}H)}_{Cu(gal\text{-}H)L}. \qquad 6$$

The stability of the mixed-ligand complexes ($CuAL$) can be quantified by comparing the difference in stability according to equation 7 [17], *i.e.* by comparing the difference in stability *e.g.* for the reaction between MA and L (A and L symbolizing the primary and secondary ligands, respectively).

$$\Delta \log K_M = \log K^{MA}_{MAL} - \log K^{M}_{ML} = \log K^{ML}_{MLA} - \log K^{M}_{MA}. \qquad 7$$

It can be observed from the results (Table 3) that the value of $\Delta \log K$ is positive in all cases, which means that ternary complexes of Cu^{2+} are more stable than the corresponding binary ones. A comparison of the stability constants (Table 3) of the mixed complexes indicates that the order of stability in terms of the secondary ligand is *sa* > *hyna* > *tsa* > *mena*. This is in accordance [18] with the basicities of the secondary ligands, the size of the ring and the nature of the donating group. On the other hand, a rough linear relationship [19] could be drawn between the values of the stability constants of these ternary systems and the second dissociation constants of the secondary ligands. The stability increases with increase of the second dissociation constant of the secondary ligands.

Experimental

Apparatus. The absorption spectra of solutions were recorded on a Perkin–Elmer (Lambda 3B) spectrophotometer in the wavelength range 200–500 nm using 1 cm matched quartz cells. Values of *pH* were measured using a Radiometer *pH*-meter (Model M63) equipped with a Radiometer combined glass electrode (GK 2301 C). Correction of *pH* readings in ethanol–water was made as described elsewhere [6]. All measurements were carried out in 40% (v/v) ethanol at 25 °C.

Chemicals and Solutions. Gallic acid, 2-hydroxy nicotinic acid (*hyna*), 2-mercapto nicotinic acid (*mena*), salicylic acid (*sa*), and thiosalicylic acid (*tsa*) were purchased from Aldrich. Spectrograde ethanol was obtained from Merck. Other Chemicals were of analytical reagent grade. All ligand solutions of initial concentration $C_L = 2.5 \times 10^{-3}\,M$ were prepared by direct weighing and dissolution in pure ethanol before use. A stock solution of copper(II) nitrate was prepared and standardized by complexometric titration [5]. The working solutions were prepared by accurate dilution. Deionized water was used throughout the present work. The acidity of solutions investigated was adjusted by the addition of either dilute nitric acid or potassium hydroxide solution. The ionic strength was maintained constant at $I = 0.1\,M$ (KNO_3).

Solutions of diverse ions used for interference studies were prepared using Analar products of the nitrate, acetate, chloride or perchlorate salts of metal ions and potassium or sodium salts of the anions to be tested.

Decomposition of Samples. A brass sample (100 mg) is dissolved in 2.5 ml of concentrated nitric acid, evaporated to dryness, extracted with 2.0 ml concentrated sulphuric acid and diluted to 100 ml. Similarly, aluminium alloy (500 mg) is dissolved in *aqua regia* and evaporated to a small volume. 5 ml of concentrated hydrochloric acid are added, and the solution is diluted to the mark with deionized water in a 50.0 ml volumetric flask. The copper content in a suitable aliquot is then determined.

Determination of Copper as its Cu-gal-sa ternary Complex. A solution containing less than 150 µg of Cu^{2+} was transferred into a 25.0 ml calibrated flask. Then 5 ml of $2.5 \times 10^{-3}\,M$ *gal* and 2.5 ml of 1.0 *M* KNO_3 were added. The *pH* was adjusted to *pH* 6.0. Then 5.0 ml of $2.5 \times 10^{-3}\,M$ *sa* were added and the solution was diluted to volume with redistilled water and the requisite amount of pure ethanol. After thorough mixing, the absorbance was measured at 420 nm against a similarly prepared reagent blank. A calibration curve with known quantities of copper was constructed similarly.

Symbols Used

C_L	Total concentration of ligand
C_M	Total concentration of metal ion
$\Delta A = A - A_L$	Differences in the overall absorbance and the absorbance of the reagent blank under the same conditions
ε_1 and ε_2	Molar absorptivities of [Cu(*gal*-H)] and [Cu(*gal*-H)*L*]
q	Number of protons released during complexation
n	Number of ligands
K_{a_1}, K_{a_2}	Acid dissociation constants of reagents
K	Equilibrium constant for the corresponding complexation reaction

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