

REACTIONS OF GALLOCYANINE METHYL ESTER  
WITH GALLIUM(III) AND INDIUM(III) IONS\*

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Reactions of gallocyanine methyl ester with gallium(III) and indium(III) ions in solutions in 15% (m/m) ethanol were studied spectrophotometrically. At pH 1.7–6.5, the  $\text{GaL}$ ,  $\text{GaL}_2$ , and  $\text{Ga}(\text{OH})\text{L}_3$  complexes are formed; in the case of indium, the  $\text{In}(\text{OH})_2\text{L}_2$  and  $\text{In}(\text{OH})\text{L}_3$  complexes appear at pH 4–6.5, and  $\text{InL}_3\text{B}_2$  in tartrate solutions. The conditional stability constants and the equilibrium constants of the coordination equilibria were calculated, and procedures were worked out for a photometric determination of gallium and for a chelatometric determination of gallium and indium using gallocyanine methyl ester as metallochromic indicator.

The not very high electronegativity of gallium and indium is manifested in their pronounced affinity to oxygen and halogens as strong electron donors. As a consequence, the trivalent ions hydrolyze readily in aqueous solutions giving rise to monomeric or polymeric hydroxo complexes or ternary hydroxo halo complexes. With organic oxygen compounds they usually form labile complexes, many of which (*e.g.*, tartrate or citrate) can be used for masking gallium or indium. Among O,O-donor ligands are also some phenoxazine dyes, of which gallocyanine has been recommended as metallochromic indicator for a determination of gallium<sup>1–3</sup>. Indium(III) ions, too, form with gallocyanine a complex, which has been studied photometrically<sup>4</sup>. Similarly as gallocyanine, its methyl ester, the so-called prune, also reacts with gallium(III) and indium(III) ions. Owing to the smaller number of the protolytic equilibria involved and the consequent higher solubility of this reagent as compared with gallocyanine itself, prune exhibits more clear-cut colour changes in reactions with ions than the parent substance.

In the present work, the coordination equilibria of gallocyanine methyl ester with gallium(III) and indium(III) ions, respectively, were studied in aqueous-methanolic solutions with the aim to find appropriate conditions for the analytical application of the reagent to a determination of these ions.

## EXPERIMENTAL

## Chemicals and Apparatus

$2 \cdot 10^{-4}\text{M}$  stock solution of gallocyanine methyl ester was prepared by dissolving the appropriate amount of substance in 93% (m/m) ethanol ( $\rho = 809.8 \text{ kg m}^{-3}$ ). The synthesis of the reagent and checking of its purity have been described<sup>5</sup>.

\* Part V in the series Complexes of Gallocyanine Methyl Ester with Inorganic Ions; Part IV: This Journal 45, 3302 (1980).

Approximately 0.01M stock solution of gallium(III) salt was prepared by dissolving a precisely weighed amount of 99.99% gallium metal (rods supplied by Závod SNP, Žiar and Hronom) in a minimal volume of concentrated HCl and diluting with water as required<sup>6</sup>. 0.01M stock solution of indium(III) salt was obtained by dissolving indium(III) nitrate (Johnson, Matthey, and Co., London) in 0.01M-HClO<sub>4</sub>. The content of indium was determined chelatometrically using xylenol orange as indicator<sup>7</sup>. This indicator was employed also in the determination of the titre of Chelaton 3 by titration with Pb(NO<sub>3</sub>)<sub>2</sub>. InAg alloy (95% (m/m) In, 5% (m/m) Ag) was supplied by Tesla, Rožnov.

The colour reaction between the metal ions and the ligand takes place instantaneously in slightly acidic solutions, but the absorbance of the solution only establishes within 15 min; then it is constant for several hours. The measurements were carried out after a 20 min period. The presence of the nonaqueous component in higher proportions is unfavourable for the coordination reaction, but, on the other hand, some amount of this component is necessary for maintaining the reagent and the complexes in solution; as a compromise, system of 15% (m/m) ethanol was used. The ionic strength in the range of  $I$  0.05–0.8 has no influence on the absorbance of the complexes, so a constant value of  $I$  0.1 was chosen (KCl for gallium, NaClO<sub>4</sub> for indium). The pH of the solution containing gallium ions was adjusted with acetate and chloro acetate buffers; in the case of indium, acetate and tartrate buffers were employed.

The pH values of the solutions were measured on a PHM 4d pH-meter fitted with the electrode system of a G 200B glass electrode and a K 100 calomel electrode (all Radiometer, Copenhagen) adjusted to potassium hydrogen phthalate aqueous solution. The pH curves in unbuffered solutions were obtained by titrations with 0.01M-NaOH or HCl using an ABU 12b automatic burette interfaced to a PHM 26 pH-meter and a TTT 11 titrator (all Radiometer, Copenhagen). The absorbances were measured on Specord UV VIS (Zeiss, Jena) and Unicam SP 1800 (Pye-Unicam, Cambridge) spectrophotometers using 1 cm cells. The photometric chelatometric titrations were accomplished on a Spekol instrument (Zeiss, Jena).

#### Data Evaluation

The composition of the complexes and their stability constants were determined from the concentration curves<sup>8,9</sup>

$$A = f(c_M)_{c_L, pH}, \quad (1)$$

the continual variations curves<sup>10</sup>

$$A = f(x)_{c_0, pH}, \quad (2)$$

and the pH-curves<sup>11</sup>

$$A = f(pH)_{c_M, c_L}, \quad (3)$$

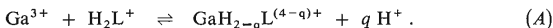
where  $c_L$  and  $c_M$  are the total analytical concentrations of the dye and the gallium(III) or indium(III) ions and  $x$  is the mole fraction of the dye ( $x = c_L/c_0$ , where  $c_0 = c_M + c_L$ ).

## RESULTS AND DISCUSSION

### Reactions of Gallium(III)

The reaction of gallium(III) ions with galloctyanine methyl ester is observable in not too acidic solutions. The blue colour appearing at pH > 1.7 changes with decreasing

acidity to violet-red. This colour change, and also the  $A = f(\text{pH})$  dependence (Fig. 1), indicates that a minimum of two coordination equilibria establish. On the absorption curves 1 for the range of pH 2–2.4 the absorption maximum displays a bathochromic shift of 24 nm ( $\lambda_{\text{max}}$  564 nm) and a low-intensity band appears at 614 nm, but a single isosbestic point is observed at 552 nm. These data, along with the continual variations curves 2 for this acidity region, reveal the occurrence of a complex with the ratio Ga : L = 1 : 1. Taking into account the prevailing concentration of the  $\text{Ga}^{3+}$  and  $\text{H}_2\text{L}^+$  species in the reaction system (83%  $\text{Ga}^{3+}$  and 94.4%  $\text{H}_2\text{L}^+$  at pH 2.4), the complex formation can be represented by the equation



With regard to the rather low stability of the complex, the conditional stability constant  $\beta'_1 = ([\text{GaL}]/\{[\text{Ga}'][\text{L}']\})$  was determined by graphical solution of the transformation equation<sup>9</sup>

$$c_L/\Delta A = 1/\Delta\varepsilon + 1/\{\beta'_1 \Delta\varepsilon(c_{\text{Ga}} - \Delta A/\Delta\varepsilon)\}, \quad (4)$$

where  $\Delta A = A - A_L$ ,  $\Delta\varepsilon = \varepsilon_C - \bar{\varepsilon}_L$ ,  $A_L = \bar{\varepsilon}_L c_L$ ,  $A = \varepsilon_C[\text{GaL}'] + \bar{\varepsilon}_L[\text{L}']$ ,  $\bar{\varepsilon}_L$  is the mean molar absorptivity of the ligand and  $\varepsilon_C$  is the molar absorptivity of the complex.

The conditional concentrations of gallium and the ligand, included in the  $\beta'_1$  constant, can be expressed by means of the coefficients of the side reactions,

$$\begin{aligned} [\text{Ga}'] &= [\text{Ga}] + [\text{Ga}(\text{OH})] + [\text{Ga}(\text{OH})_2] = \\ &= [\text{Ga}] (1 + Q_1[\text{H}]^{-1} + Q_2[\text{H}]^{-2}) = [\text{Ga}] \alpha_{\text{Ga}(\text{OH})}, \end{aligned} \quad (5)$$

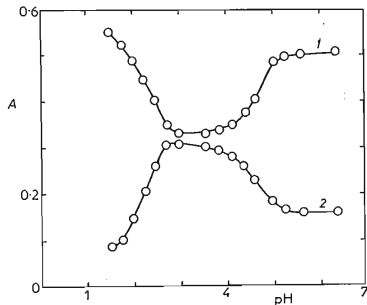


FIG. 1

Dependence of absorbance on the pH of solutions of prune and gallium(III).  $c_L = c_{\text{Ga}} = 2 \cdot 10^{-5} \text{ mol l}^{-1}$ , 15% (m/m) ethanol,  $d = 1 \text{ cm}$ . 1 502 nm, 2 642 nm

where  $Q$ 's are the hydrolytic constants<sup>12</sup> ( $Q_1 = \text{Ga}(\text{OH})_i [\text{H}]^i / [\text{Ga}]$ ;  $Q_1 = 10^{-3.09}$ ,  $Q_2 = 10^{-6.64}$ ,  $Q_3 = 10^{-11.04}$ ,  $Q_4 = 10^{-17.09}$ ),

$$[\text{L}'] = [\text{H}_2\text{L}] + [\text{HL}] = [\text{H}_2\text{L}] (1 + K_{a1}[\text{H}]^{-1}) = [\text{H}_2\text{L}] \alpha_{\text{L}(\text{H})}, \quad (6)$$

where  $K_{a1}$  is the dissociation constant of the reagent ( $K_{a1} = 10^{-3.63}$  for 15.5% (m/m) ethanol<sup>13</sup>). The dependence of  $\log(\beta'_1 \alpha_{\text{Ga}(\text{OH})} \alpha_{\text{L}(\text{H})})$  on pH in the range pH 2–2.4 is linear and corresponds to the splitting-off of two protons ( $q = 2$ ). Thus the  $^*\beta_1$  constant of reaction (A) can be written as

$$^*\beta_1 = [\text{GaL}][\text{H}]^2 / \{[\text{Ga}][\text{H}_2]\} \quad (7)$$

or

$$^*\beta_1 = \beta'_1 \alpha_{\text{Ga}(\text{OH})} \alpha_{\text{L}(\text{H})} [\text{H}]^2 \quad (8)$$

and its value is given in Table I.

The equilibrium constants  $^*\beta_1$  were also calculated from the pH-curves (3) according to the relation

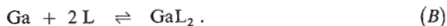
$$\begin{aligned} \log \{ (A - A_1)(A_{\text{max}} - A_L) \alpha_{\text{Ga}(\text{OH})} \alpha_{\text{L}(\text{H})} / (A_{\text{max}} - A)^2 \} = \\ = \log ^*\beta_1 + 2 \text{pH} + \log c_L, \end{aligned} \quad (9)$$

where  $A_{\text{max}} = \epsilon c_L$ . The  $^*\beta_1$  constants calculated in the two ways are in a good mutual agreement (Table I). The presumed equilibrium (A) for  $q = 2$  can be thus looked upon as the likely mechanism of the GaL binary complex formation.

Changes in the solution composition appear at acidities as high as pH > 2.5. On the absorption curves 1, the absorption maximum of the ligand decreases, and subsequently there appears a flat maximum the complex at 515–534 nm and an isosbestic point at  $\lambda_{\text{iso}}$  604 nm. As the metal ion concentration is raised ( $c_{\text{Ga}} > c_L/2$ ), the maximum shifts in the direction of higher wavelengths to 564 nm (Fig. 2), a value characteristic of the GaL complex. The absorption curves thus indicate a simultaneous occurrence of two complexes with the ratios Ga : L = 1 : 1 and 1 : 2. The higher complex was found only in a narrow pH range, most pronounced at pH 2.94. For this pH and the isosbestic point wavelength 526 nm was calculated the conditional stability constant  $\beta'_2$ ,

$$\beta'_2 = [\text{GaL}'_2] / ([\text{Ga}'] [\text{L}']^2), \quad (10)$$

characterizing the equilibrium



The conditional concentrations of the  $\text{GaL}_2$  complex and the corresponding absorbances are interrelated through the equation<sup>8</sup>

$$[\text{GaL}'_2]/[\text{GaL}'_2]_{\max} = A_{\text{GaL}_2}/A_{\max}, \quad (11)$$

TABLE I

Conditional stability and equilibrium reaction constants for the system Ga(III)-galloyanine methyl ester (15% (m/m) ethanol, 1:0.1)

pH	<i>n</i>	$\log \beta'_n$	$\log * \beta_n$	$l \text{ mol}^{-1} \text{ cm}^{-1}$	$\lambda$ nm	Equilibrium
1.9–2.5 <sup>a</sup>	1	—	$0.46 \pm 0.04$	$1.92 \cdot 10^4$	518	A
1.9–2.5 <sup>a</sup>	1	—	$0.48 \pm 0.07$	$2.25 \cdot 10^4$	614	A
1.9–2.5 <sup>a</sup>	1	—	$0.52 \pm 0.05$	$1.35 \cdot 10^4$	670	A
2.15 <sup>b</sup>	1	4.74	0.50	—	—	A
2.24 <sup>b</sup>	1	4.90	0.50	$2.35 \cdot 10^4$	564	A
2.40 <sup>b</sup>	1	5.14	0.45	—	—	A
2.94 <sup>c</sup>	2	11.35	—	$4.15 \cdot 10^4$	526	B
4.65 <sup>d</sup>	3	17.39	13.07	—	—	C
4.98 <sup>d</sup>	3	17.75	12.96	—	—	C
5.77 <sup>c</sup>	3	18.55	12.99	$6.27 \cdot 10^4$	502	C
5.80 <sup>d</sup>	3	18.54	12.96	—	—	C
6.20 <sup>d</sup>	3	18.87	13.07	—	—	C

<sup>a</sup> Calculation from the pH-curves (3), the average of 7 values of  $*\beta$  converted to the logarithm, the confidence interval determined for 95% probability; <sup>b</sup> calculation by transformation<sup>9</sup> from the concentration curves (1); <sup>c</sup> calculation from the concentration curves (1) according to Kleiner<sup>8</sup>; <sup>d</sup> calculation from the continual variations curves<sup>10</sup> (2); the  $\beta'_1$  and  $\beta'_3$  constants of the equilibria A and C are averages of five values for different wavelengths and converted to the logarithms.

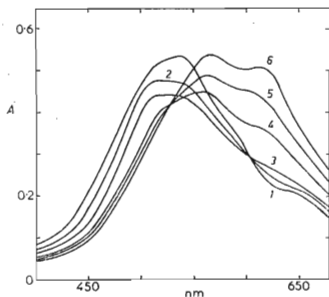


FIG. 2

Absorption curves of prune and gallium(III) solutions.  $c_L = 2 \cdot 10^{-5} \text{ mol l}^{-1}$ , pH 2.94, 15% (m/m) ethanol,  $d = 1 \text{ cm}$ , 1:0.1.  $c_{\text{Ga}}$  ( $\text{mol l}^{-1}$ ): 1 0, 2  $0.32 \cdot 10^{-5}$ , 3  $0.5 \cdot 10^{-5}$ , 4  $2 \cdot 10^{-5}$ , 5  $4 \cdot 10^{-5}$ , 6  $6 \cdot 10^{-5}$

where  $A_{\max} = \epsilon_{C_2} c_L / 2$  and  $\epsilon_{C_2}$  is the molar absorptivity of the  $\text{GaL}_2$  complex. For  $\epsilon_{\text{Ga}} = 0$  and  $d = 1$  cm we have

$$A_{\text{GaL}_2} = A - A_L = A - (c_L - 2[\text{GaL}'_2]) \bar{\epsilon}_L. \quad (12)$$

Inserting in Eq. (11) and putting  $[\text{GaL}'_2]_{\max} = c_L / 2$  we obtain a relation for the equilibrium concentration of the complex,

$$[\text{GaL}'_2] = (c_L / 2) \{ (A - A_L) / (A_{\max} - A_L) \}. \quad (13)$$

The remaining equilibrium concentrations are

$$[\text{Ga}'] = c_{\text{Ga}} - [\text{GaL}'_2] \quad (14)$$

and

$$[\text{L}'] = c_L - 2[\text{GaL}'_2]. \quad (15)$$

The conditional stability constant  $\beta'_2$  of the  $\text{GaL}_2$  complex was calculated from Eqs (10), (13)–(15); the value is given in Table I. Since the complex formation mechanism is unknown, the corresponding equilibrium constant could not be evaluated.

In the range  $\text{pH} > 3.2$  appears an additional complex with the ratio  $\text{Ga} : \text{L} = 1 : 3$ . This complex, which at  $\text{pH} > 4.5$  is the only coordination compound left in the solution and, according to Fig. 1, is completed near  $\text{pH} 6$ , is manifested on the  $A = f(c_{\text{Ga}})_{c_L, \text{pH}, 1}$  curves by an absorption maximum at 502 nm and a single isosbestic point at 552 nm over a wide span of gallium concentration ( $c_{\text{Ga}} = (0 - 5) c_L$ ,  $c_L = 2 \cdot 10^{-5} \text{ mol l}^{-1}$ ). The equilibrium was confirmed by the continual variations and the molar ratios methods. For establishing the conditional constant  $\beta'_3$ ,

$$\beta'_3 = [\text{GaL}'_3] / ([\text{Ga}'] [\text{L}']^3), \quad (16)$$

the general equation of the Job curve<sup>10</sup> for a 1 : 3 complex was employed:

$$(1 - x - y)(x - 3y)^3 - (1/\beta'_3 c_0^3) y = 0, \quad (17)$$

where  $c_0 = c_{\text{Ga}} + c_L$ ,  $x = c_L / c_0$ , and  $y = [\text{GaL}'_3] / c_0$ . The absorbance, or the Job function  $Y$ , is proportional to the concentration of the complex and thereby also to the function  $y$ :

$$|Y| = \epsilon d c_0 y. \quad (18)$$

In the case of a quantitative complex formation,  $y$  attains the limiting value of 0.25, and the  $Y_0$  function is

$$|Y_0| = 0.25\varepsilon dc_0, \quad (19)$$

where  $\varepsilon = |\varepsilon_C - 3\varepsilon_L|$ . From the ratio of these functions in the point of the maximum on the continual variations curve we obtain

$$y_{\max} = 0.25(|Y|_{\max}/|Y_0|_{\max}), \quad (20)$$

permitting  $\beta'_3$  to be calculated either from Eq. (17) for  $x = 0.75$  or from the graphical representation of the dependence  $y = f\{\log(\beta'_3 c_0^3)\}$  whose values, obtained from a computer, have been tabulated<sup>10</sup>.

The values of the conditional stability constant  $\beta'_3$  were also derived from the concentration ratios curves by the method of Kleiner<sup>9</sup>. Applying relations (11)–(13), the concentrations of the complex and of its constituents were expressed as

$$[\text{GaL}'_3] = (c_L/3) \{(A - A_L)/(A_{\max} - A_L)\} \quad (21)$$

$$[\text{Ga}'] = c_{\text{Ga}} - [\text{GaL}'_3] \quad (22)$$

and

$$[\text{L}'] = c_L - 3[\text{GaL}'_3]. \quad (23)$$

These relations then were inserted in Eq. (16) to give the  $\beta'_3$  constant. In the examined range pH 4.5–6.2, the conditional concentration of ligand is

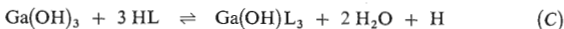
$$\begin{aligned} [\text{L}'] &= [\text{H}_2\text{L}] + [\text{HL}] + [\text{L}] = \\ &= [\text{HL}] ([\text{H}] K_{a1}^{-1} + 1 + [\text{H}]^{-1} K_{a2}) = [\text{HL}] \alpha_{\text{L(H)}}. \end{aligned} \quad (24)$$

The nondissociated HL species is highly predominating (90.3% at pH 4.6 and 98.6% and pH 6.2), and hence will take part in the complex formation. As to gallium, the hydrolytic species  $\text{Ga}(\text{OH})_3$  prevails (its maximum is 77.6% at pH 5.2), so

$$\begin{aligned} [\text{Ga}'] &= [\text{GaOH}] + [\text{Ga}(\text{OH})_2] + [\text{Ga}(\text{OH})_3] + [\text{Ga}(\text{OH})_4] = \\ &= [\text{Ga}(\text{OH})_3] \{Q_1 Q_3^{-1} [\text{H}]^2 + Q_2 Q_3^{-1} [\text{H}] + 1 + Q_4 Q_3^{-1} [\text{H}]^{-1}\} = \\ &= [\text{Ga}(\text{OH})_3] \alpha_{\text{Ga(OH)}}. \end{aligned} \quad (25)$$

The dependence of  $\log(\beta'_3 \alpha_{\text{Ga(OH)}} \alpha_{\text{L(H)}}^3)$  on pH is linear over the acidity range in question, with the slope of unity. This fact, combined with the assumption of a simple

formalism of  $[Ga'] \equiv [Ga(OH)_3]$  and  $[L'] \equiv [HL]$ , allows us to represent the coordination equilibrium by the equation



characterized by the constant

$$*\beta_3 = [Ga(OH)L_3][H]/([Ga(OH)_3][HL]^3). \quad (26)$$

This constant then is related to the conditional stability constant through

$$*\beta_3 = \beta_3^* [H] \alpha_{Ga(OH)} \alpha_{L(H)}^3 \quad (27)$$

and is given in Table I.

### Photometric Determination of Gallium

At pH  $\sim 6$ , the stability of  $Ga(OH)L_3$  is high enough to permit its utilization in photometric determination of gallium. The appropriate wavelength, with the highest  $\epsilon_{HL} - \epsilon_{C_3}$  difference, is 640 nm. At  $c_L = 2 \cdot 10^{-5} \text{ mol l}^{-1}$  and  $I 0.1$ , Beer's law is obeyed for gallium concentrations not exceeding  $0.4 \mu\text{g/ml}$ . The sensitivity of determination is  $1.2 \text{ ng Ga/cm}^2$  (for  $A = 0.001$ ). The relative standard deviation for  $55.6 \text{ ng Ga/ml}$  and 10 replicate determinations is  $s_r = 3.64\%$ . Ions of  $In^{3+}$ ,  $Pb^{2+}$ ,  $Th^{4+}$ ,  $Zr^{4+}$ ,  $Fe^{3+}$ ,  $Ni^{2+}$ ,  $Zn^{2+}$ ,  $Bi^{3+}$ ,  $Ge(IV)$ , and  $Sn(IV)$  interfere. The accuracy of the results was verified by the  $t$ -test for the level of significance  $\alpha = 0.05$  with respect to the actual value  $\xi = 1.390 \mu\text{g Ga/25 ml}$ ; only random errors were involved ( $t_{exp} < t_{crit}$ ) (ref.<sup>14</sup>).

**Procedure:** To a mixture of 12.5 ml of acetate buffer (pH 5.8–6,  $I 0.1$ ), 2.5 ml of  $2 \cdot 10^{-4} \text{ M}$  ethanolic solution of prune, and 2.5 ml of 93% (m/m) ethanol in a 25 ml volumetric flask is added 1–10  $\mu\text{g Ga(III)}$ , and the solution is brought to volume with water. The absorbance is measured after 15 min.

### Chelatometric Determination of Gallium

Direct chelatometric determination of gallium with prune as indicator is conducted in chloroacetate buffer solution (pH  $\sim 2.5$ ). The colour change is from blue to violet-red. The blue complex reacts with EDTA rather reluctantly, it is therefore convenient to heat up the solution and to titrate slowly near the equivalence point. The optimum amount of indicator is 1.5–2 ml of  $2 \cdot 10^{-4} \text{ M}$  ethanolic solution, the titrant solution is 0.001–0.002M-EDTA; 0.5–50 mg of Ga can be determined with a relative error typically below 1%. The relative standard deviation for 440.3  $\mu\text{g}$  and five replicate determinations is  $s_r = 2.94\%$ . As little as 50  $\mu\text{g}$  Ga can be determined applying photometric indication of the titration end point.

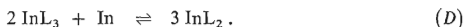


Indirectly can the determination be accomplished by titrating excess chelaton with  $\text{Th}(\text{NO}_3)_4$ ; the colour change at pH 2.5 is from violet-red to blue.

Ions of  $\text{In}^{3+}$ ,  $\text{Th}^{4+}$ ,  $\text{Zr}^{4+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Fe}^{3+}$  interfere with the chelatometric determination of gallium. The accuracy was verified by the *t*-test for the probability level of 95%; only random errors were involved<sup>14</sup>.

### Reactions of Indium(III)

Indium salts react with galloxyanin methyl ester only in solutions with pH > 3.5 giving rise to violet colour; the absorbance is constant at pH > 5. The absorption maximum is shifted by as much as 147 nm to shorter wavelengths ( $\lambda_{\text{max}}$  497 nm) as compared with that of the ligand, and the curves 1 intersect in an isosbestic point at 546 nm. These values characterize a complex with the ratio In : L = 1 : 3. As the metal ion concentration is increased, a rounded peak appears on the absorption curves 1 with the maximum at 526 nm, due to another complex with the ratio In : L = 1 : 2; the isosbestic point at 505 nm (Fig. 3) characterizes the equilibrium



As compared with galloxyanin<sup>4</sup>, which forms with indium(III) ions a single, not very stable  $\text{InL}_2$  complex ( $\lambda_{\text{max}}$  496 nm,  $\epsilon_c = 2.3 \cdot 10^3$ , pH 4.85), its methyl ester exhibits a higher coordination ability, due to a lower polarization of the molecule at the given pH and to the consequent lower hydration.

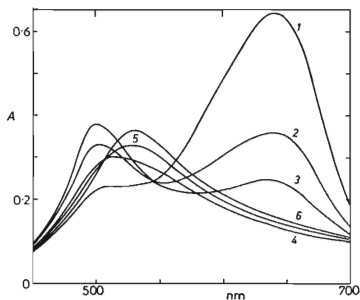


FIG. 3  
Absorption curves of prune and indium(III) solutions.  $c_L = 2 \cdot 10^{-5} \text{ mol l}^{-1}$ , pH 5.30, 15% (m/m) ethanol,  $d = 1 \text{ cm}$ ,  $I = 0.1$ .  $c_{\text{In}}$  ( $10^{-5} \text{ mol l}^{-1}$ ): 1 0, 2 0.4, 3 0.6, 4 1.5, 5 2, 6 2.5

The higher complex,  $\text{InL}_3$ , is the predominating species in solution, showing up in the dependences (1) and (2) over the entire region pH 4–6.5 at all wavelengths. The continual variations curves at  $\lambda < 590$  nm are distorted due to the occurrence of the  $\text{InL}_2$  complex, so that for the determination of the  $\text{InL}_3$  complex, higher wavelengths had to be used for obtaining the Job function values. The applicability of the continual variations method to the calculation of the conditional stability constants  $\beta'_3$  was tested by plotting the  $y = f(x)$  dependence using Eq. (18). The tangent from the point  $x = 1$  attains its maximum,  $y = 0.25$ , at  $x = 0.75$ , and is parallel to the tangent calculated from the general equation<sup>15</sup> (for an  $\text{M}_m\text{L}_n$  complex)

$$y = -(1/m)x + (n-1)/\{m(m+n-1)\} \quad \text{for } n \geq 2. \quad (28)$$

In this manner the fact was proved that at selected wavelengths ( $\lambda > 590$  nm) only the  $\text{InL}_3$  complex manifests itself, and so the  $\beta'_3$  constants could be determined by Klausen's modification<sup>10</sup> of the calculation from the continual variations curves according to Eqs (17)–(20). In addition, the constants were calculated also from the concentration curves using relations (16), (21)–(23), whereby the correctness of the above approach was confirmed.

If present in low concentrations, indium ions are hydrolyzed practically only to monodentate hydroxo compounds<sup>12</sup>, and so in the acidity region pursued, four species can be regarded as making up the conditional concentration of indium:

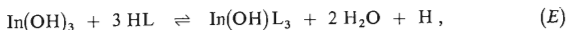
$$[\text{In}'] = [\text{In}] + [\text{InOH}] + [\text{In(OH)}_2] + [\text{In(OH)}_3], \quad (29)$$

the last of them being highly predominant (91% at pH 5.62) and thus constituting also the principal reactant. Eq. (29) then can be modified to

$$[\text{In}'] = [\text{In(OH)}_3] (Q_3^{-1}[\text{H}]^3 + Q_1 Q_3^{-1}[\text{H}]^2 + Q_2 Q_3^{-1}[\text{H}] + 1) = [\text{In(OH)}_3] \alpha_{\text{In(OH)}} \quad (30)$$

with the hydrolytic constants  $Q_1 = 10^{-4.49}$ ,  $Q_2 = 10^{-8.55}$ , and  $Q_3 = 10^{-13.14}$  (ref.<sup>12</sup>).

The dependence of  $\log(\beta'_3 \alpha_{\text{In(OH)}} \alpha_{\text{L(H)}}^3)$  on pH in which the conditional concentration of ligand is expressed by Eq. (24) is linear over the region in question, and for the formalism  $[\text{L}'] \equiv [\text{HL}]$  and  $[\text{In}'] \equiv [\text{In(OH)}_3]$  the coordination equilibrium can be regarded as



with the corresponding constant

$$*\beta_3 = [\text{In(OH)L}_3][\text{H}]/\{[\text{In(OH)}_3][\text{HL}]^3\}, \quad (31)$$

or

$$*\beta_3 = \beta'_3[\text{H}] \alpha_{\text{In(OH)}} \alpha_{\text{L(H)}}^3, \quad (32)$$

where  $\beta'_3 = [\text{In(OH)L}_3]/\{[\text{In}'][\text{L}']^3\}$ . The values are given in Table II.

The lower complex,  $\text{InL}_2$ , formed if the metal ions are present in excess, was evaluated based on the concentration curves (1) at  $\lambda_{\text{iso}}$  546 nm. For  $\epsilon_{\text{In}} = 0$  and  $d = 1$  cm,

$$A_{\text{InL}_2} = A - A_{\text{InL}_3} = A - (c_L - 2[\text{InL}_2]) \epsilon_{\text{C3}}/3. \quad (33)$$

Substituting into Eq. (11) and putting  $[\text{InL}'_2]_{\text{max}} = c_L/2$  we obtain

$$[\text{InL}'_2] = (c_L/2) \{(A - A_{\text{InL}_3}) / (A_{\text{max}} - A_{\text{InL}_3})\}. \quad (34)$$

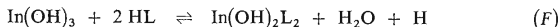
TABLE II

Conditional stability constants and equilibrium reaction constants for the system In(III)-gallo-cyanine methyl ester (15% (m/m) ethanol, 1:0.1)

pH	<i>n</i>	$\log \beta'_n$	$\log * \beta_n$	$l \text{ mol}^{-1} \text{ cm}^{-1}$	$\lambda$ nm	Equilibrium
5.30 <sup>a</sup>	2	12.46	7.26	$1.18 \cdot 10^4$	546	F
5.95 <sup>a</sup>	2	13.20	7.28	—	—	F
6.27 <sup>a</sup>	2	13.55	7.29	$2.39 \cdot 10^4$	546	F
4.80 <sup>a</sup>	3	16.35	11.88	—	—	E
4.95 <sup>a</sup>	3	16.15	11.44	—	—	E
5.30 <sup>a</sup>	3	17.03	11.84	—	—	E
5.62 <sup>b</sup>	3	16.89	11.34	—	—	E
5.95 <sup>a</sup>	3	17.73	11.82	$2.55 \cdot 10^4$	500	E
6.25 <sup>b</sup>	3	17.57	11.35	—	—	E
4.94 <sup>a</sup>	3	15.26	5.45	—	—	G
5.10 <sup>a</sup>	3	15.83	5.67	—	—	G
5.29 <sup>b</sup>	3	15.94	5.39	—	—	G
5.55 <sup>b</sup>	3	16.65	5.57	—	—	G
5.55 <sup>a</sup>	3	16.63	5.55	$8.82 \cdot 10^4$	500	G
6.00 <sup>b</sup>	3	17.56	5.57	—	—	G
6.80 <sup>a</sup>	3	19.22	5.68	—	—	G

<sup>a</sup> Calculation from the concentration curves (1); <sup>b</sup> calculation from the continual variations curves (2); the  $\beta'_n$  constants of the equilibria E and G are averages for five wavelengths and converted to the logarithms.

The conditional stability constant  $\beta'_2$  was calculated based on Eqs (10), (14), (15), and (34). The dependence of  $\log(\beta'_2 \alpha_{\text{In(OH)}} \alpha_{\text{L(H)}}^2)$  on pH is linear, also with a slope of unity. Thus, similarly as in the preceding case, the coordination equilibrium can be written as



characterized by the equilibrium constant

$$*\beta_2 = [\text{In(OH)}_2\text{L}_2][\text{H}] / \{[\text{In(OH)}_3][\text{HL}]^2\}, \quad (35)$$

or

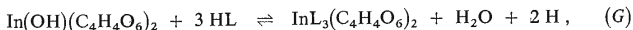
$$*\beta_2 = \beta'_2[\text{H}] \alpha_{\text{In(OH)}} \alpha_{\text{L(H)}}^2, \quad (36)$$

whose values are given in Table II.

In chelatometric determinations of indium, use is frequently made of salts of organic hydroxy acids<sup>3</sup>, particularly tartrates or citrates, which by complex formation prevent hydrolysis of the metal ion at higher pH values and formation of side products. Such systems are useful also in the reaction of indium(III) with prune, which then is well-defined. By graphical analysis of dependences (1) and (2) the occurrence was proved of a single complex with the ratio In : L = 1 : 3, characteristic by the spectral values  $\lambda_{\text{max}}$  497 nm and  $\lambda_{\text{iso}}$  546 nm. Obviously, the hydroxy acid anion not only prevents separation of hydrolysis products, but also takes part in the formation of the multicomponent system. As a consequence, the molar absorptivity  $\epsilon_{\text{C}_3}$  is nearly four times as high as that observed in acetate buffer solution free of tartrate.

When the alkali salt of the hydroxy acid is present in a constant high excess,  $c_{\text{B}} > 100(c_{\text{In}} + c_{\text{L}})$  (B is the hydroxy acid anion), the system is well buffered and, moreover, can be looked upon as pseudobinary, since  $[\text{InL}_3] = [\text{InL}_3\text{B}_r]$  and so the conventional methods for binary equilibria can be applied. The conditional stability constants for the  $\text{InL}_3$  complex in tartrate solutions were established from the concentration curves based on Eqs (16), (21)–(23), and from the continual variations curves by the procedure (17)–(20).

The indium(III) ions form with tartrate a complex, which at  $\text{pH} > 3$  transforms into the stable hydroxo derivative<sup>16,17</sup>  $\text{In(OH)(C}_4\text{H}_4\text{O}_6)_2^{2-}$  and in the reaction with gallocyanine methyl ester will be the only reacting species of the metal ion. The slope  $q = 2$  of the linear dependence of  $\log(\beta'_3 \alpha_{\text{L(H)}}^3)$  on pH suggests that on the action of an additional ligand, the hydroxy group and the coordination-bonded water in the indium–tartrate complex are substituted and the  $\text{InL}_3(\text{C}_4\text{H}_4\text{O}_6)_2^{4-}$  ternary complex is formed according to the scheme



characterized by the constant

$$\begin{aligned} * \beta_{32} &= [\text{InL}_3\text{B}_2][\text{H}]^2 / \{[\text{In}(\text{OH})\text{B}_2][\text{HL}]^3\} = \\ &= \beta'_{32} \alpha_{\text{L}(\text{H})}^3 [\text{H}]^2 \end{aligned} \quad (37)$$

given in Table II (B is the tartrate anion).

### Chelatometric Determination of Indium

Tartrate solutions proved to suit well for chelatometric determination of indium using galloycyanine methyl ester as indicator. The colour change from violet to blue is sharpest at pH 5–5.5, and can be monitored visually or photometrically. With a relative error below 1%, 0.1–50 mg In can be determined visually (relative standard deviation  $s_r = 4.15\%$  for 119.5  $\mu\text{g}$  In and five replicate determinations) and 0.05 to 50 mg In can be determined photometrically ( $s_r = 6.85\%$  for 50.5  $\mu\text{g}$  In and five replicate determinations). Chelatometric titration using xylenol orange as indicator<sup>7</sup> served as the reference method. Ions of  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  in traces and  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ln}^{3+}$ ,  $\text{Ga}^{3+}$ ,  $\text{UO}_2^{2+}$  in quantities equal to or exceeding the indium content interfere.

*Procedure:* To a sample containing 0.05–50 mg In are added 10 ml of 0.1M tartaric acid and 1 ml of  $2 \cdot 10^{-4}\text{M}$  ethanolic solution of prune. The optimum acidity, pH  $\sim 5.2$ , is adjusted with 0.2M-NaOH using a Phan indicator paper (Lachema, Brno). After making up to the volume of 30–40 ml, the system is titrated with 0.01M-EDTA solution.

The chelatometric determination of indium was successfully applied to an alloy containing about 5% (m/m) silver. The latter had to be removed from the reaction mixture as  $\text{AgCl}$ , because the  $\text{Ag}^+$  ion increases the consumption of reagent. The accurate content of indium in the alloy was unknown. The confidence interval was therefore calculated<sup>14</sup> from the range  $R$  and the Lord's distribution coefficient  $K_n$ :

$$L_{1,2} = \bar{x} \pm K_n R, \quad (38)$$

where  $\bar{x}$  is the arithmetic mean of the results. Outliers were excluded based on the Dean-Dixon test<sup>14</sup>. Five replicate determinations afforded the confidence interval  $L_{1,2} = (94.68 \pm 0.34)\%$  In for the level of significance  $\alpha = 0.05$ , demonstrating the applicability of the method to the determination of indium in this material.

*Procedure:* 100–150 mg of the InAg alloy containing 95% (m/m) In is dissolved in a minimal volume of concentrated  $\text{HNO}_3$ , and the solution is gently evaporated to dryness. The residue is taken up in 10–20 ml of water, and 1 ml of 0.01M-HCl is added. The  $\text{AgCl}$  precipitate is filtered off and washed, and the filtrate is brought to volume of 100 ml with water in a volumetric flask. One ml of this stock solution is pipetted into a titration flask, 10 ml of 0.1M sodium potassium

tartrate is added and the solution is diluted with the same volume of water. After adding 1 ml of  $2 \cdot 10^{-4}$  M ethanolic solution of prune and adjusting pH  $\sim 5.2$  with approximately 0.1 ml of 0.1 M tartaric acid, the system is titrated with 0.02 M-EDTA to blue colour.

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