

REACTIONS OF GALLOCYANINE METHYL ESTER WITH GERMANIUM(IV), TIN(IV) AND LEAD(II) IONS*

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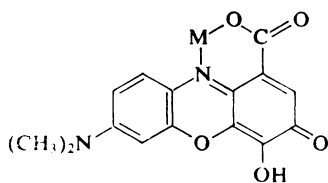
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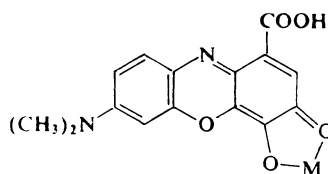
The reactions of gallocyanine methyl ester with germanium(IV) and tin(IV) in 7.7% (m/m) ethanol and with lead(II) in 15.5% (m/m) ethanol are studied spectrophotometrically. In slightly acid solutions, complexes of GeL_3 (pH 2.5–6.5), SnL_2 and SnL_3 (pH 1.7–6 in the presence of tartaric acid), and PbL and PbL_2 (pH 4–7) are formed. The conditional stability constants of the complexes and the equilibrium constants of the complexation reactions are calculated and procedures are suggested for the photometric determination of tin and for the chelometric determination of lead using visual or photometric indication with gallocyanine methyl ester as metallochromic indicator (colour change from red-violet to blue). A gallocyanine methyl ester-methyl orange screened indicator proved useful for the visual determination of lead, showing an expressive colour change from brown to green.

Elements of the germanium group show a pronounced affinity for electron donors. In agreement with the electronegativity values after Allred and Rochow¹ (Ge 2.02, Sn 1.72, Pb 1.55) the covalent nature of the M–O bond increases in the series $\text{Pb} < \text{Sn} < \text{Ge}$. As a consequence, the hydrolyzability of the ions in aqueous solutions increases markedly in this series, monomeric and polymeric soluble or insoluble hydroxo complexes being formed. The affinity for oxygen also shows up in the reactivity with organic ligands, particularly hydroxy compounds. Of some phenoxazine dyes which are O,O'-donor ligands, florein² and gallocyanine^{3–6} have been used for the detection and determination of lead^{2–4} and germanium^{5,6}.

Two sites in gallocyanine are potentially free for the complexation of metal ions⁷:



I



II

* Part VII in the series Complexes of Gallocyanine Methyl Ester with Inorganic Ions; Part VI: This Journal 49, 2070 (1984).

Of the two, structure *II* is the more likely. This is corroborated by reactions of Modern Violet (4-hydroxy-7-dimethylaminophenoxaz-3-one, C.I. 51025), which differs from gallocyanine only in that the hydrogen in position 1 is not substituted by a functional group. The only complexing grouping thus is 4-hydroxy-3-carbonyl (Type *II*). The reactivity of the reagent with Ge(IV) is more pronounced as compared with gallocyanine and the detection of germanium is four times more sensitive^{5,6}. Structure *II* is also borne out by reactions of gallocyanine methyl ester, so-called prune, with some inorganic ions^{8,9}. This reagent reacts with the same ions as gallocyanine itself or Modern Violet. Owing to its higher solubility as compared with the parent compound, its colour changes are more expressive and thus of more analytical utility. The aim of the present work was to investigate the reactions of gallocyanine methyl ester with Ge(IV), Sn(IV), and Pb(II) ions in aqueous-ethanolic solutions and to seek for the optimum conditions for the application of the reagent to the determination of these ions.

EXPERIMENTAL

Solutions and Apparatus

A stock solution of gallocyanine methyl ester (prune, C.I. 51040) in a concentration of 0.2 mmol l^{-1} was prepared by dissolving the chemical in 93% (*m/m*) ethanol. The preparation and testing of its purity have been described previously¹⁰.

A stock solution of germanium(IV) ($c_{Ge} = 5 \text{ mmol } l^{-1}$) was obtained by dissolving GeO_2 *p.p.* (Lachema, Brno) in 50 ml of 1.5% (*m/m*) NaOH and diluting to 250 ml with water. A 20 ml aliquot was neutralized with 15 ml of 0.1M-HCl and diluted to 50 ml with water to obtain a solution containing germanium in a concentration of 2 mmol l^{-1} . A stock solution of tin(IV) salt was prepared by dissolving 0.8–0.9 g of tin metal *p.a.* (Lachema, Brno) in 25 ml of hot concentrated sulphuric acid. After cooling down, the solution was added to 150 ml of ice-cool distilled water. A tenfold concentration excess of tartaric acid was added to suppress hydrolysis, and the whole was diluted with water to 250 ml. By neutralization and dilution with water, a concentration of 1 mmol l^{-1} was obtained. A solution of $Pb(NO_3)_2$ in a concentration of 20 mmol l^{-1} was prepared by dissolving the dry salt *p.a.* (Lachema, Brno) in 0.01M- $HClO_4$.

Urotropine, acetate, and chloroacetate buffers were used for the pH adjustment. Ionic strength, which over the region of 1.0–0.1–0.5 did not affect significantly the absorbance of the complexes, was held at a constant value of 1.0 for all measurements, using KCl for germanium and $NaClO_4$ for tin and lead.

The pH measurements were performed on a PHM 4d pH-meter using a system of a G 200B glass electrode and a K 100 calomel electrode (all Radiometer, Copenhagen) standardized by means of aqueous solutions of potassium hydrogenphthalate. The absorbances were measured on a Unicam SP 1800 spectrophotometer (Pye Unicam, Cambridge) in 1 cm and 2 cm cells. The absorbance-pH curves in unbuffered systems were obtained by titration with 0.01M-HCl or NaOH using an ABU 12b automatic burette interfaced to PHM 26 pH-meter and a TTT 11 titrator (all Radiometer, Copenhagen). The titrant was added directly to the sample cell of a volume of 100 ml, optical path length $d = 3.5 \text{ cm}$, clamped in a special holder after Karlíček¹¹, manufactured at the workshop of the Faculty of Pharmacy in Hradec Králové. For the pH monitoring, an electrode system of a 40498 glass electrode (Beckman) and a K 401 calomel electrode (Radio-

meter) was inserted into the sample cell through the adapted lid¹¹ of the cell compartment. The cell contents were homogenized by nitrogen for lamps, whose flow rate was controlled with a needle valve. This titration system was employed also for obtaining the concentration ratios curves with variable amounts of the metal ions, added from a burette. The absorption curves were recorded 1 min after discontinuing the nitrogen feed. The photometric determinations and the photometric chelometric titrations were performed with a Spekol spectrophotometer (Carl Zeiss, Jena).

Evaluation of Experimental Data

The composition and the stability constants of the complexes were determined from the concentration curves¹²⁻¹⁴

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

and the absorbance-pH curves¹⁵

$$A = f(pH)_{c_M, c_L, l}, \quad (2)$$

where c_M and c_L are the total concentrations of the metal ion and ligand, respectively.

RESULTS AND DISCUSSION

Germanium(IV)

The formation of the violet colour in the reaction of germanium(IV) with galloyanine methyl ester is controlled by three principal factors, *viz* the solution acidity (pH 2.5–6.5), time of colour development, and concentration of ethanol. The absorbance establishes only in 40 min and then is steady for several hours. The ethanol content of the solutions is of importance. A minimal concentration is necessary for sustaining the homogeneous system, the absorbance in the maximum of the complex, however, decreases with increasing methanol concentration. The optimum value 7.7% (*m/m*) ethanol, was obtained by a tenfold dilution of the ethanol stock solution of ligand.

The absorption curves of the solutions with a constant concentration of ligand and variable concentration of the metal ion ($c_{Ge} = (0-5) c_L$) at pH 3.5–6.0 exhibit the formation of a flat maximum at 520–580 nm ($\lambda_{max, H_2L} = 534$ nm, $\lambda_{max, HL} = 642$ nm) and a single isobestic point at 565 nm. The assumption of the occurrence of a single coordination equilibrium was confirmed by the concentration ratio curves. Regarding the considerable dissociation of the complex, the coefficients of the reaction were determined *via* the transformation equation¹³

$$(c_L/\Delta A) = (n/\Delta \epsilon) + 1/[\beta'_{mn} \Delta \epsilon (c_M - m \Delta A/\Delta \epsilon)^m \Delta A^{n-1}]^{1/n} \quad (3)$$

derived from the general equation for the conditional stability constant,

$$\beta'_{mn} = (\Delta A/\Delta \epsilon) / [(c_M - m \Delta A/\Delta \epsilon)^m (c_L - n \Delta A/\Delta \epsilon)^n], \quad (4)$$

where $\Delta A = A - \bar{\epsilon}_L c_L$, $\Delta \epsilon = \epsilon_C - n\bar{\epsilon}_L$, ϵ_C is the molar absorptivity of the $M_m L_n$ complex, and $\bar{\epsilon}_L$ is the mean molar absorptivity of ligand; $\epsilon_M = 0$.

The plots of the dependence $c_L/\Delta A = f\{1/[(c_{Ge} - \Delta A/\Delta \epsilon) \Delta A^{n-1}]^{1/n}\}$ for $m = 1$, $n = 1-3$ revealed the formation of a single complex, GeL_3 , over the entire region used (Fig. 1). The $\Delta \epsilon$ value, and thus also ϵ_C , was calculated accurately by extrapolation of the linear function ($n = 3$), and the conditional stability constants β'_3 were obtained from the slope and also from Eq. (4).

In the pH 1.6–7.0 range, $Ge(IV)$ is completely hydrolyzed and a single species^{16,17} $Ge(OH)_4$, or $Ge(OH)_4(H_2O)_2$, predominates. Hence, the simple formalism $[Ge'] \equiv [Ge(OH)_4(H_2O)_2] = [Ge]$ can be adopted. The conditional concentration of ligand includes the two acid species,

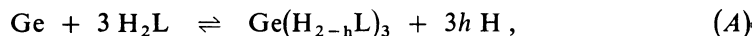
$$[L'] = [H_2L^+] + [HL] = [H_2L^+](1 + K_{a1}/[H^+]), \quad (5)$$

or

$$[L'] = [HL] (1 + [H^+]/K_{a1}) \quad (6)$$

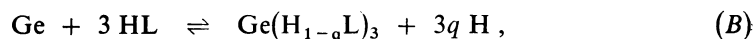
($K_{a1} = 10^{-3.68}$ and $K_{a2} = 10^{-7.99}$ in 7.7% (m/m) ethanol¹⁸).

The coordination equilibrium involving the two protolytic forms of ligand then can be formulated generally as



$$**\beta_3 = [Ge(H_{2-h}L)_3][H]^{3h}/\{[Ge][H_2L]^3\} \quad (7a)$$

$$**\beta_3 = \beta'_3(1 + K_{a1}/[H])^3 [H]^{3h}; \quad (7b)$$



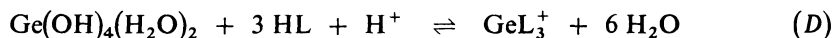
$$*\beta = [Ge(H_{1-q}L)_3][H]^{3q}/\{[Ge][HL]^3\} \quad (8a)$$

$$*\beta_3 = [Ge(H_{1-q}L)_3][H]^{3q}/\{[Ge][HL]^3\} \quad (8a)$$

$$*\beta_3 = \beta'_3(1 + [H]/K_{a1})^3 [H]^{3q}. \quad (8b)$$

The dependence $\log \{\beta'_3(1 + K_{a1}/[H])^3\} = f(\text{pH})$ is linear with a slope of $q = 2$ for the entire region of pH 3.5–6.0. This implies that $h = 2/3$. The dependence of $\log \{\beta'_3(1 + [H]/K_{a1})^3\} = f(\text{pH})$ is also linear, the slope is $q = -1$, hence, $q =$

= $-1/3$. So the equilibria (A) and (B) can be specified as



and the equilibrium constants are interrelated through

$$**\beta_3 = * \beta_3 K_{a1}^3. \quad (9)$$

In view of the increasing concentration of the HL species with increasing pH (40% at pH 3.5 and 99.5% at pH 6.0), equilibrium (D) can be expected to prevail, with the constant

$$* \beta_3 = [\text{GeL}_3^+] / \{ [\text{Ge(OH)}_4(\text{H}_2\text{O})_2] [\text{HL}]^3 [\text{H}] \}, \quad (10)$$

the values of which are given in Table I.

For elucidating the equilibrium, the absorbance-pH curves (Eq. (2)) were also used (Fig. 2). The absorbance, for $d = 1$ cm, is

$$A = \varepsilon_c [\text{GeL}_3^+] + \bar{\varepsilon}_L [\text{HL}] (1 + [\text{H}]/K_{a1}). \quad (11)$$

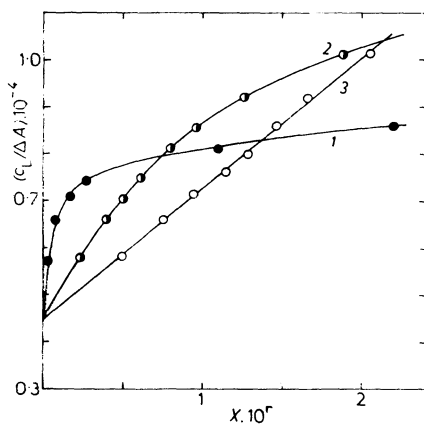


FIG. 1

Ketelaar's transformation (3) of the $A = f(c_{\text{Ge}})$ curves; $c_L = 20 \mu\text{mol l}^{-1}$, pH 4.45, 7.7% (m/m) ethanol, $I 0.1$, $\lambda 642$ nm, 1 cm cells. $X = 1 / [(c_{\text{Ge}} - \Delta A / \Delta \varepsilon) \Delta A^{n-1}]^{1/n}$. n, r : 1 1, 6; 2 2, 3; 3 3, 2

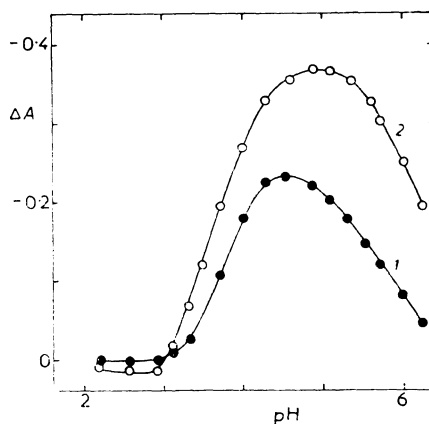


FIG. 2

Absorbance-pH curves for the germanium (IV)-galloyanine methyl ester system in 7.7% (m/m) ethanol, $I 0.1$; $c_L = 20 \mu\text{mol l}^{-1}$, $d = 1$ cm, $\lambda 642$ nm. $\Delta A = A - A_L$, c_{Ge} ($\mu\text{mol l}^{-1}$): 1 10, 2 100

Since the total concentrations are

$$c_{Ge} = [Ge] + [GeL_3] \quad (12)$$

and

$$c_L = [HL] (1 + [H]/K_{a1}) + 3 [GeL_3], \quad (13)$$

the constant for equilibrium (*D*) can be written as

$$\begin{aligned} {}^*\beta_3 &= \frac{(A - A_L)(A_{max} - A_L)^3}{[3pA_{max} - A - (3p - 1)A_L](A_{max} - A)^3} \cdot \frac{(1 + [H]/K_{a1})^3}{[H]c_L^3} = \\ &= Z(1 + [H]/K_{a1})^3 / \{[H]c_L^3\}, \quad (14) \end{aligned}$$

where $p = c_{Ge}/c_L$, $A_L = \bar{\epsilon}_L c_L$, $A_{max} = \epsilon_C c_L/3$. All plots of $\log \{Z(1 + [H]/K_{a1})^3\}$ vs pH for $p = 0.5$ or 5.0 and for various wavelengths are linear with a slope of $\rho = -1$, which confirms the assumed mechanism (*D*). The values of the ${}^*\beta_3$ constants (Table II) agree with those derived from the concentration curves.

The rather long time necessary for the absorbance to establish, together with the similar course of the reactions of germanium(IV) with some hydroxycarbonyl compounds such as hydroxyparones, hydroxyquinones, or β -diketones^{19,20}, indicates

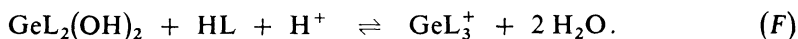
TABLE I

Conditional stability constants and equilibrium constants for the germanium(IV)-gallocyanine methyl ester system in 7.7% (*m/m*) ethanol, *I* 0.1

pH	$\log \beta_3'^a$	$\log {}^*\beta_3$	ϵ_C (550 nm) $10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$
3.50	14.63	19.33	5.50
3.67	14.81	19.40	—
3.85	14.80	19.32	—
4.00	14.83	19.34	5.45
4.13	14.85	19.38	—
4.28	14.85	19.42	—
4.45	14.80	19.45	5.47
4.59	14.71	19.45	—
4.80	14.55	19.44	—
4.96	14.43	19.46	5.45
5.40	13.88	19.36	—
5.53	13.80	19.33	5.37

^a Logarithm of the average β_3' value obtained from five measurements at different wavelengths

that mechanism (D) is the resultant of the stepwise complexation



The two acid hydrogens of germanic acid are used up in the condensation of water in reaction (E), and so the reaction proceeds with no change in pH. The coordination of the next ligand is associated with the uptake of a proton (F). Reaction (F) is partly suppressed by higher pH, and this together with the decomposition of the $\text{GeL}_2(\text{OH})_2$ complex due to the dissociation of the components and hydrolysis of the metal ion results in a decrease in the stability of the GeL_3^+ complex (Fig. 2, β'_3 value in Table I).

The stability constants β'_3 of the GeL_3 complex are comparatively low, and so the equilibrium cannot be employed with advantage for the spectrophotometric determination of germanium.

TABLE II

Equilibrium constants calculated from the absorbance-pH curves (2) for the germanium(IV)-galloxyaniline methyl ester system in 7.7% (m/m) ethanol, I 0.1

pH	<i>p</i>	$\log * \beta_3^a$	λ nm	ϵ_C^b $10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$
3.0–6.0	0.5	19.55	490	4.65
	5.0	19.54		
2.9–6.0	0.5	19.51	534	5.30
	5.0	19.49		
3.4–6.2	0.5	19.57	610	3.49
	5.0	19.53		
3.2–6.0	0.5	19.59	642	2.95
	5.0	19.57		
3.6–6.0	0.5	19.56	670	1.87
	5.0	19.53		

^a Logarithm of the average $*\beta_3$ value obtained from 10–11 measurements and calculations by Eq. (14); ^b Obtained from the concentration ratios curves (1).

Tin(IV)

The study of the coordination equilibria is aggravated by the hydrolysis of tin(IV) ions, which even at pH 0–1 leads to the formation of a precipitate²¹ of Sn(OH)₄, or SnO₂·x H₂O. To prevent the precipitation, a tenfold concentration excess of tartaric acid was added to the tin(IV) salt solution. The complex compound formed reacts with prune over the pH 1.7–6 range giving rise to red-violet colour, which establishes in 45 min and remains steady for several hours. Ethanol has an unfavourable effect on the complexation, similarly as was the case with germanium; its concentration was therefore held again at the lowest value possible, *viz.* 7.7% (m/m).

The solution composition is simplest in slightly acid systems, at pH 5–6. The absorption curves (1) display a single isosbestic point at 578 nm, and the absorption maximum of the complex (at 562 nm) is 80 nm shifted to shorter wavelengths with respect to the maximum of the free ligand. The concentration ratios curves confirmed the occurrence of a single complex, SnL₂. The conditional stability constant $\beta'_2 = [\text{SnL}'_2]/([\text{Sn}'][\text{L}'^2])$ can be calculated based on the relation

$$[\text{SnL}'_2]/[\text{SnL}'_2]_{\text{max}} = A_C/A_{\text{max}}, \quad (15)$$

where $A_C = A - A_L$ and A_{max} is the absorbance at $c_{\text{Sn}} \gg c_L$ ($\epsilon_{\text{Sn}} = 0$).

At $c_L = \text{const}$ we have

$$[\text{SnL}'_2] = (c_L/2) A_C/A_{\text{max}}. \quad (16)$$

Since $A_L = (c_L - 2[\text{SnL}'_2]) \bar{\epsilon}_L d$, Eq. (16) can be written as

$$[\text{SnL}'_2] = (c_L/2) \{(A - A_L)/(A_{\text{max}} - A_L)\}. \quad (17)$$

Inserting Eq. (17) in the relation for β'_2 under the condition $c_{\text{Sn}} = c_L/2$ and rearranging we obtain the final relation

$$\beta'_2 = (A - A_L)(A_{\text{max}} - A_L)^2 / \{(A_{\text{max}} - A)^3 c_L^2\}. \quad (18)$$

With the excess tartaric acid the tartrate complex of tin can be assumed to be the only metal species present; so we can write $[\text{Sn}'] = [\text{Sn}(\text{tar})_x] = [\text{Sn}]$. Using Eq. (6), the plot of the dependence $\log \{\beta'_2(1 + [\text{H}]/K_{a1})^2\} = f(\text{pH})$ is a straight line with a zero slope. It is clear that the hydrogen ions of ligand are released in the form of water in the coordination reaction. The equilibrium can be written as



defined by the constant

$$\beta_2 = [\text{Sn}(\text{OH})_{p-2}\text{L}_2(\text{tar})_x] / \{[\text{Sn}(\text{OH})_p(\text{tar})_x][\text{HL}]^2\}, \quad (19a)$$

or

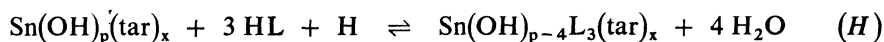
$$\beta_2 = \beta'_2(1 + [\text{H}]/K_{a1})^2, \quad (19b)$$

the values of which are given in Table III along with the values of β'_2 .

In more acidic solutions, pH 3.1–4.5, the absorption curves (I) for $c_{\text{Sn}} = (0-8) c_L$ exhibit two equilibria characterized by three isosbestic points at 574, 486, and 636 nm at pH 4.02 (Fig. 3), 572, 492, and 638 nm at pH 3.60, and 570, 510, and 650 nm at pH 3.10. The concentration ratios curves revealed the presence of complexes of the composition Sn : L = 1 : 2 and 1 : 3. The stability of the latter complex was determined from the longest-wavelength isosbestic points. The procedure of Eqs (15)–(17) provided the relation for the conditional stability constant β'_3 ,

$$\beta'_3 = (A - A_L)(A_{\text{max}} - A_L)^3 / \{(A_{\text{max}} - A)^4 c_L^3\} \quad (20)$$

($c_L = \text{const}$). The dependence $\log \{\beta'_3(1 + [\text{H}]/K_{a1})^3\} = f(\text{pH})$ is linear with a slope of $\varrho = -1$, corresponding to the uptake of a proton in the coordination reaction



defined by the equilibrium constant

$$*\beta_3 = [\text{Sn(OH)}_{p-4}\text{L}_3(\text{tar})_x] / \{[\text{Sn(OH)}_p(\text{tar})_x][\text{HL}]^3[\text{H}]\}, \quad (21a)$$

TABLE III

Conditional stability constants, equilibrium constants, and molar absorptivities ϵ_{C2} at 562 nm and ϵ_{C3} at 638 nm ($10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$) for the tin(IV) – galloycyanine methyl ester system in 7.7% (m/m) ethanol, I 0.1

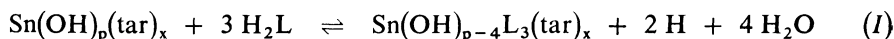
pH	$\log \beta'_2$	$\log \beta_2$	$\log \beta'_3$	$\log * \beta_3$	ϵ_{C2}	ϵ_{C3}
3.10	11.40 ^a	12.76	18.06	23.20	—	—
3.60	12.10 ^a	12.75	18.65	23.27	5.38	4.60
4.02	12.41 ^a	12.74	18.77	23.28	—	4.62
5.02	13.12 ^b	13.16	—	—	4.60	—
5.20	13.17 ^b	13.20	—	—	4.76	—
5.34	13.16 ^b	13.18	—	—	4.50	—
5.65	13.17 ^b	13.18	—	—	4.68	—
5.90	13.19 ^b	13.19	—	—	4.62	—

^a Calculated according to Eq. (31); ^b calculated according to Eq. (18).

or

$$*\beta_3 = \beta'_3(1 + [H]/K_{a1})^3/[H]. \quad (21b)$$

With regard to the fact that while the SnL_3 complex is also formed in more acidic solutions containing excess protonated form of ligand, H_2L^+ ($\text{p}K_{a1} = 3.68$), it does not appear at $\text{pH} > 5$, the equilibrium



can be also assumed. The corresponding equilibrium constant is

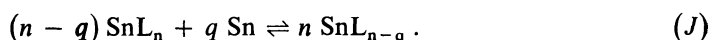
$$**\beta_3 = [\text{Sn(OH)}_{p-4}\text{L}_3(\text{tar})_x][\text{H}]^2/\{[\text{Sn(OH)}_p(\text{tar})_x][\text{H}_2\text{L}]^3\}, \quad (22a)$$

or

$$*\beta_3 = \beta'_3(1 + [H]/K_{a1})^3 [\text{H}]^2. \quad (22b)$$

Again, the $\log \{\beta'_3(1 + K_{a1}/[H])^3\} = f(\text{pH})$ dependence is linear, its slope is 2. Equilibria (H) and (I) are equivalent, their constants being interrelated through Eq. (9).

For a quantitative handling of the equilibria of the complex with fewer ligands occurring together with the SnL_3 complex and persisting as the only one at $\text{pH} > 5$, the assumption of the conversion of the higher complex into the lower taking place with increasing concentration of metal ion was adopted:



The total concentrations of the reactants are

$$c_{\text{Sn}} = [\text{Sn}'] + [\text{SnL}_{n-q}] + [\text{SnL}_n] \quad (23)$$

$$c_{\text{L}} = (n - q) [\text{SnL}_{n-q}] + n [\text{SnL}_n] \quad (24)$$

($[\text{L}] \approx 0$); the absorbance in the isosbestic point in the 570 nm range (for $d = 1$ cm) is given by

$$A = \varepsilon_{n-q}[\text{SnL}_{n-q}] + \varepsilon_n[\text{SnL}_n]. \quad (25)$$

Combining Eqs (24) and (25) we obtain

$$[\text{SnL}_{n-q}] = (A - \varepsilon_n c_{\text{L}}/n)/\{\varepsilon_{n-q} - \varepsilon_n(n - q)/n\} = \Delta A/\Delta \varepsilon. \quad (26)$$

The conditional stability constant of reaction (J) is

$$K'_{n,n-q} = [\text{SnL}_{n-q}]^n / \{[\text{SnL}_n]^{n-q} [\text{Sn}]^q\}, \quad (27)$$

and Eqs (23), (24), and (26) provide the relation

$$K'_{n,n-q} = (n \Delta A / \Delta \varepsilon)^n / \{[c_L - (n - q) \Delta A / \Delta \varepsilon]^{n-q} [nc_{\text{Sn}} - c_L - q \Delta A / \Delta \varepsilon]^q\}, \quad (28)$$

a linear transformation of which gives

$$c_L / \Delta A = (n - q) / \Delta \varepsilon + \{(n / \Delta \varepsilon)^n (1 / K'_{n,n-q}) [\Delta A / (nc_{\text{Sn}} - c_L - q \Delta A / \Delta \varepsilon)]^q\}^{1/(n-q)}. \quad (29)$$

An approximate value of ε_{n-q} can be derived from the concentration ratios curves. After substitution in Eq. (29), the true value is obtained from the plot of the dependence $c_L / \Delta A = f\{[\Delta A / (nc_{\text{Sn}} - c_L - q \Delta A / \Delta \varepsilon)]^q\}$ and again substituted in Eq. (29). With the n and q values correctly chosen, viz. $n = 3$ and $q = 1$, the graphical dependence has a linear shape (Fig. 4). Equilibrium (J) and Eq. (27) thus can be

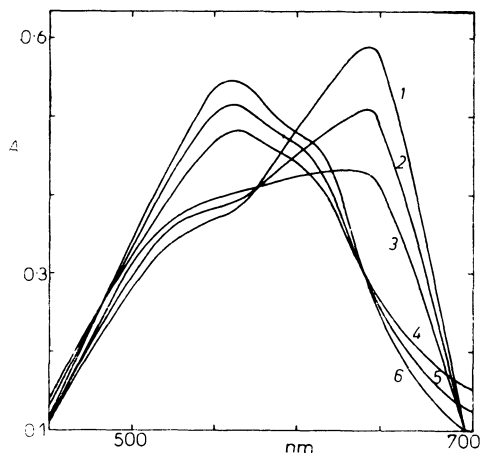


FIG. 3

Absorption curves for the tin(IV)-gallocyanine methyl ester system in 7.7% (m/m) ethanol, $I 0.1$; $c_L = 6 \mu\text{mol l}^{-1}$, pH 4.02, $d = 3.5$ cm. $c_{\text{Sn}} (\mu\text{mol l}^{-1})$: 1 0, 2 0.6, 3 1.2, 4 6.0, 5 24.0, 6 48.0

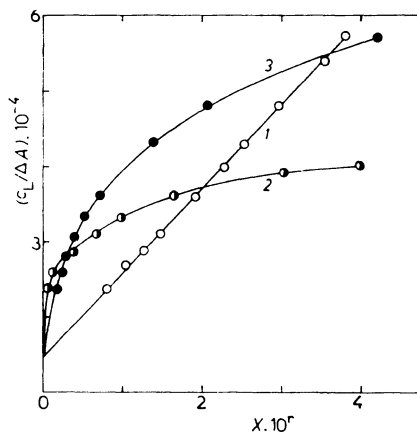
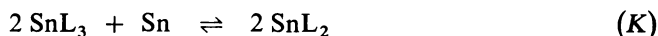


FIG. 4

Transformation (29) of the $A = f(c_{\text{Sn}})$ curves; $c_L = 6 \mu\text{mol l}^{-1}$, pH 3.10, 7.7% (m/m) ethanol, $I 0.1$, $\lambda 570$ nm, $d = 1$ cm. $X = [\Delta A / (nc_{\text{Sn}} - c_L - q \Delta A / \Delta \varepsilon)]^q / (n - q)$. n, q, r : 1 3, 1, 1; 2 3, 2, 5; 3 2, 1, 3

written in the particular forms



$$K'_{3,2} = [\text{SnL}_2]^3 / \{[\text{SnL}_3]^2 [\text{Sn}]\} . \quad (30)$$

The slope of the transformed function (29), or relation (28), enables the equilibrium constant $K'_{3,2}$ to be calculated and converted to the conditional stability constant of the SnL_2 complex *via* the relation

$$\beta'_2 = (\beta'_3 K'_{3,2})^{1/3} . \quad (31)$$

The equilibrium constant β_2 for reaction (G), calculated by Eq. (19b), is given in Table III.

Two complexes, SnL_2 and SnL_3 , are also formed in the pH 1.7–2.8 range. The absorption curves (I) intersect in two isosbestic points, at 558 and 530 nm (pH 2.60) or 554 and 540 nm (pH 2.10). As the concentration of the metal ion is increased over the region $c_{\text{Sn}} = (0-0.3) c_{\text{L}}$, the absorption intensity in the maximum of the ligand (534 nm) decreases and the maximum of the SnL_3 complex formed is 10 nm shifted to longer wavelengths. If the metal ions concentration is further increased, the maximum at 544 nm is additionally shifted to longer wavelengths and increased in intensity. The new absorption maximum at 562 nm is due to the SnL_2 complex. Since the absorbance differences in the isosbestic points and the maxima of the complexes and ligands are too low, the equilibria could not be followed accurately enough in this acidity range.

Photometric Determination of Tin(IV)

At pH 5–6 the stability of the SnL_2 complex in excess tartaric acid is high enough to enable its application to the photometric determination of tin(IV). The optimum wavelength, at which the $\epsilon_{\text{HL}} - \epsilon_{\text{C}}$ difference is highest, is 642 nm. With $c_{\text{L}} = 20 \mu\text{mol l}^{-1}$, about 8% (m/m) ethanol, ionic strength I 0.1, and pH 5.5 (acetate buffer), Beer's law is obeyed at concentrations $\zeta_{\text{Sn}} < 0.9 \text{ mg l}^{-1}$; the regression equation describing the dependence of absorbance (y) on the concentration of tin in mg l^{-1} (x) is $y = 0.5908 - 1.1413x$. The relative standard deviation for five replicate determinations of tin in a concentration of 0.38 mg l^{-1} was 1.82%. The accuracy was tested by the t -test on the $\alpha = 0.05$ significance level and only random errors were found to be involved ($t_{\text{exp}} < t_{\text{crit}}$, ref.²²). Ions of Ag^+ , Ga^{3+} , In^{3+} , Fe^{3+} , Zr^{4+} , Th^{3+} , Bi^{3+} , Pb^{2+} , Al^{3+} , Hg^{2+} , Ni^{2+} , Cd^{2+} , Cu^{2+} , Ge(IV), and molybdates and vanadates interfere.

Procedure. To an acid sample of tin(IV) salt is added tartaric acid in an approximately tenfold excess, the solution is neutralized with NaOH (indication with a universal pH-paper) and diluted

to a defined volume. To a 25 ml volumetric flask are added 2.5 ml of ethanolic solution of prune ($c_L = 0.2 \text{ mmol l}^{-1}$), 10 ml of acetate buffer pH ≈ 5.5 ($I 0.1$), and a volume of the solution prepared, containing 1.5–20 $\mu\text{g Sn(IV)}$, and the mixture is diluted to volume with water. In 45 min the absorbance at 642 nm is measured against a blank.

Lead(II)

Lead(II) salts react with prune in slightly acid solutions, pH 4–7. The absorbance of the violet solutions drops with time and precipitate appears in 24 h. For sustaining the complex in solution, the ethanol content had to be doubled (15.5% (m/m)) and the ligand concentration had to be lowered to $c_L = 6 \mu\text{mol l}^{-1}$. In this solution the absorbance established in 5 min and was steady for an hour.

The absorbance-pH curves (2) indicate a stepwise complex formation with changing acidity and at different proportions of the reactants (Fig. 5). A single complexation equilibrium was found in acid region of pH 4.3–6.1. The maximum of the complex, at 572 nm, is 70 nm shifted to longer wavelengths with respect to the maximum of the free ligand. The coordination equilibrium is characterized by isosbestic points at 582 and 688 nm. The concentration curves revealed the occurrence of the PbL complex, which was also confirmed by the linear transformation (3); complexes with the component ratios 1 : 2 or 2 : 2 are rejected.

The conditional stability constant β'_1 at pH 4.51–5.38 was calculated from Eq. (4), substituting for $\Delta\varepsilon$ from the transformation (3) for $m = n = 1$, whereas Kleiner's method¹⁴ was used for the pH 5.66–6.08 range. The relation

$$\beta'_1 = (A - A_L)(A_{\text{max}} - A_L) / \{(A_{\text{max}} - A_L)^2 c_L\} \quad (32)$$

was derived by procedure Eqs (15)–(17) and substitution in the relation for β'_1 at $c_L = c_M$.

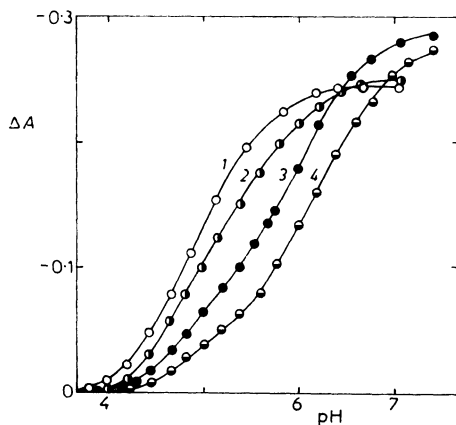
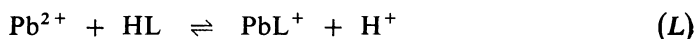


FIG. 5

Absorbance-pH curves for the lead(II)-gallo-cyanine methyl ester system in 15.5% (m/m) ethanol, $I 0.1$; $c_L = 6 \mu\text{mol l}^{-1}$, $\lambda 642 \text{ nm}$, $d = 2 \text{ cm}$. $\Delta A = A - A_L$. c_{Pb} ($\mu\text{mol l}^{-1}$): 1 24.0, 2 12.0, 3 6.0, 4 3.0

The plot of $\log \{\beta'_1(1 + [H]/K_{a1})\}$ vs pH is a straight line with a slope of unity, and characterizes the simple coordination equilibrium



defined by the constant

$${}^*\beta_1 = [\text{PbL}][\text{H}]/\{[\text{Pb}][\text{HL}]\}, \quad (33a)$$

or

$${}^*\beta = \beta'_1(1 + [H]/K_{a1}) [H]. \quad (33b)$$

The results agree well with the data calculated from the absorbance-pH curves (Fig. 5). Combining Eqs (11)–(13) adapted to the PbL complex with Eq. (33) we obtain

$$\log \{Z(1 + [H]/K_{a1})\} = \log {}^*\beta_1 + \log c_L + \text{pH}, \quad (34)$$

where $Z = (A - A_L)(A_{\max} - A_L)/\{[pA_{\max} - A - (p - 1)A_L](A_{\max} - A)\}$, $p = c_{\text{Pb}}/c_L \geq 1$, $A_{\max} = \varepsilon_C c_L d$ (ε_C determined from the concentration curves), or

$$\log \{Y(1 + [H]/K_{a1})\} = \log {}^*\beta_1 + \log (qc_{\text{Pb}}) + \text{pH}, \quad (35)$$

where $Y = (A - A_L)(qA_{\max} - A_L)/\{[A_{\max} - A + (1 - 1/q)A_L](qA_{\max} - A)\}$, $q = c_L/c_{\text{Pb}} \geq 1$, $A_{\max} = \varepsilon_C c_{\text{Pb}} d$ (ε_C determined from the concentration curves).

The two dependences, Eqs (34) and (35), bear out the suggested mechanism (L); the values of the constants are given in Table IV.

In less acid solutions (pH > 6) another equilibrium establishes, apparent on the absorption curves (1) at pH 6.5–7 ($\lambda_{\text{iso},1}$ 572 and 696 nm, $\lambda_{\text{iso},2}$ 530 nm). The stepwise coordination reaction leading to the PbL and PbL₂ complexes is evident from both the concentration ratios curves and the pH curves (Fig. 5). Kleiner's modification of the concentration ratios method¹⁴ was used again for the calculation of the conditional stability constant of the PbL₂ complex

$$\beta'_2 = [\text{PbL}_2]/\{[\text{Pb}'][\text{L}']^2\} \quad (36)$$

at the wavelength of the isobestic point at 530 nm (at $c_{\text{Pb}} < c_L/2$). At $c_{\text{Pb}} = c_L/2$ we have

$$[\text{PbL}_2] = (c_L/2) A_C/A_{\max} \quad (c_L = \text{const}) \quad (37)$$

$$[\text{Pb}'] = c_{\text{Pb}} - [\text{PbL}_2] \quad (38)$$

$$[\text{L}'] = c_L - 2[\text{PbL}_2]. \quad (39)$$

The stability constant β'_2 then can be calculated by inserting from Eqs (37)–(39) in Eq. (36), or by means of Eq. (18).

The conditional concentrations of the metal ions and ligand, included in the β'_2 constants, can be expressed *via* the coefficients of the side reactions,

$$\begin{aligned} [\text{Pb}'] &= [\text{Pb}] + [\text{Pb}(\text{OH})] + [\text{Pb}(\text{OH})_2] + [\text{Pb}(\text{OH})_3] = \\ &= [\text{Pb}] (1 + \beta_1^{\text{OH}}[\text{OH}] + \beta_2^{\text{OH}}[\text{OH}]^2 + \beta_3^{\text{OH}}[\text{OH}]^3) = [\text{Pb}] \alpha_{\text{Pb}(\text{OH})}, \\ [\text{L}'] &= [\text{HL}] + [\text{L}'] = [\text{HL}] (1 + K_{a2}/[\text{H}]) = [\text{HL}] \alpha_{\text{L}(\text{H})}, \end{aligned} \quad (41)$$

where β^{OH} are the stability constants of the hydroxo complexes in aqueous solutions¹⁷ ($\beta_i^{\text{OH}} = [\text{Pb}(\text{OH})_i]/\{[\text{Pb}][\text{OH}]^i\}$; $\beta_1^{\text{OH}} = 10^{6.04}$, $\beta_2^{\text{OH}} = 10^{10.64}$, $\beta_3^{\text{OH}} = 10^{13.94}$) and K_{a2} is the 2nd dissociation constant of reagent ($K_{a2} = 10^{-8.10}$ for 15.5% (*m/m*))

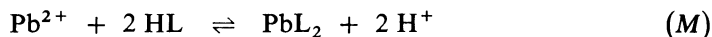
TABLE IV

Conditional stability constants, equilibrium constants, and molar absorptivities ϵ_{C1} at 572 nm and ϵ_{C2} at 530 nm ($10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$) for the lead(II) — gallocyanine methyl ester system in 15.5% (*m/m*) ethanol, *I* 0.1

pH	$\log \beta'_1$	$\log * \beta_1$	$\log \beta'_2$	$\log * \beta_2$	<i>p</i>	<i>q</i>	ϵ_{C1}	ϵ_{C2}
4.5–6.0	—	0.03 ^a	—	—	4	—	—	—
4.5–6.0	—	0.08 ^a	—	—	2	—	—	—
4.7–5.7	—	0.07 ^a	—	—	—	1	—	—
4.7–5.5	—	0.12 ^a	—	—	—	2	—	—
4.51	4.61 ^b	0.15	—	—	—	—	—	—
5.03	5.17 ^b	0.16	—	—	—	—	2.40	—
5.36	5.51 ^b	0.15	—	—	—	—	—	—
5.66	5.78 ^c	0.12	—	—	—	—	2.50	—
5.87	6.03 ^c	0.16	—	—	—	—	2.52	—
6.08	6.23 ^c	0.15	—	—	—	—	2.48	—
6.60	6.18 ^d	−0.41	11.77 ^e	−1.38	—	—	—	3.71
6.78	6.31 ^d	−0.42	12.15 ^e	−1.34	—	—	2.45	3.73
7.00	6.52 ^d	−0.40	12.53 ^e	−1.36	—	—	2.45	3.65

^a Calculated from the absorbance-pH curves, Eq. (34) or (35); ^b logarithm of the average β'_1 value obtained from 5 values calculated from the concentration curves (*I*) by Eq. (4); ^c logarithm of the average β'_1 obtained from 5 values for different wavelengths calculated from the concentration curves (*I*) by Eq. (32); ^d calculated by Eq. (44) for 572 nm wavelength; ^e calculated from the concentration curves (*I*) by Eq. (18) or Eqs (36)–(39) for 530 nm wavelength

ethanol¹⁸). The $\log(\beta'_2 \alpha_{\text{Pb(OH)}} \alpha_{\text{L(H)}}^2) = f(\text{pH})$ dependence is linear and corresponds to the substitution of two protons. Regarding the highly predominant concentrations of the Pb^{2+} and HL species (80% Pb^{2+} , 20% PbOH , 93% HL, at pH 7), the coordination equilibrium can be written as



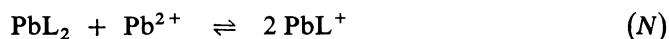
and defined by the constant

$$*\beta_2 = [\text{PbL}_2][\text{H}]^2 / \{[\text{Pb}][\text{HL}]^2\}, \quad (42a)$$

or

$$*\beta_2 = \beta'_2 \alpha_{\text{Pb(OH)}} \alpha_{\text{L(H)}}^2 [\text{H}]^2. \quad (42b)$$

The parallel formation of the PbL complex at pH 6.5–7 can be expressed as



with the constant

$$K'_{2,1} = [\text{PbL}]^2 / \{[\text{PbL}_2][\text{Pb}']\}, \quad (43)$$

by means of which the conditional stability constants β'_1 and β'_2 can be interrelated as

$$\beta'_1 = (\beta'_2 K'_{2,1})^{1/2}. \quad (44)$$

The $K'_{2,1}$ value was calculated from the absorbances and the total concentrations of the species present in the isosbestic point at 572 nm (for $c_{\text{Pb}} \geq c_{\text{L}}/2$) of the molar ratios curves.

$$A = \varepsilon_{\text{C}_1}[\text{PbL}] + \varepsilon_{\text{C}_2}[\text{PbL}_2] \quad (d = 1 \text{ cm}) \quad (45)$$

$$c_{\text{L}} = [\text{PbL}] + 2[\text{PbL}_2] \quad ([\text{L}] \approx 0) \quad (46)$$

$$c_{\text{Pb}} = [\text{Pb}'] + [\text{PbL}] + [\text{PbL}_2]. \quad (47)$$

Combining Eqs (45) and (46) we obtain

$$[\text{PbL}] = (2A - \varepsilon_{\text{C}_2} c_{\text{L}}) / (2\varepsilon_{\text{C}_1} - \varepsilon_{\text{C}_2}), \quad (48)$$

and substituting from Eqs (46)–(48) in (43) and rearranging,

$$K'_{2,1} = 2(A - A_2)^2 / \{(A_1 - A) [(p - 1/2) A_1 + (1 - p) A_2 - A/2]\}, \quad (49)$$

where $p = c_{\text{Pb}}/c_{\text{L}}$, $A_1 = \varepsilon_{\text{C}_1}c_{\text{L}}$, and $A_2 = \varepsilon_{\text{C}_2}c_{\text{L}}/2$ (for $d = 1$ cm). The conditional stability constant β'_1 of the PbL complex then was calculated from Eq. (44). The $^*\beta_1$ constant for equilibrium (L) at pH 6.5–7 was determined by means of equation

$$^*\beta_1 = \beta'_1 \alpha_{\text{Pb(OH)}} \alpha_{\text{L(H)}} [\text{H}] ; \quad (50)$$

the values are given in Table IV.

Chelometric Determination of Lead(II)

The chelometric determination of lead is performed in urotropine buffer solutions (pH \approx 5.5). The colour change is from red-violet to blue. For making the colour change sharper it is convenient to use a screened indicator of prune with methyl orange; the colour change then is from brown to green. The optimum amount is 1.5 to 2 ml of a $2 \cdot 10^{-4}$ M ethanolic solution of prune with 3 drops of 0.1% (m/m) methyl orange; the titrant solution is 0.002–0.02 M-EDTA. In this manner, 2–40 mg Pb can be determined visually with a relative error lower than 1%. The relative standard deviation for five replicate determinations of 2.07 mg Pb was 1.51%, or 0.99% using the screened indicator. As little as 0.4 mg Pb can be determined using photometric indication of the end point at 640 nm. The relative standard deviation for five replicate determinations of 0.414 mg Pb was $s_r = 1.93\%$.

Ions of Fe^{3+} , Th^{4+} , Zr^{4+} , In^{3+} , Ga^{3+} , Bi^{3+} , Al^{3+} , Cu^{2+} , Cd^{2+} , Zn^{2+} , Hg^{2+} , and Ge(IV) interfere. The accuracy was subjected to the t -test for the $\alpha = 0.05$ significance level. Only random errors were involved.

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REFERENCES

1. Gažo J., Kohout J., Serátor M., Šramko T., Zikmund M.: *Všeobecná a anorganická chemia*, p. 687. Alfa, Bratislava 1974.
2. Lasovský J., Růžička E.: *Mikrochim. Acta* 1972, 467.
3. Pavelka F.: *Mikrochemie* 7, 301 (1929).
4. Dubský J. V., Chodák L.: *This Journal* 11, 523 (1938).
5. Tchakirian A., Bevilard P.: *C. R., Acad. Sci.* 233, 256, 1033 (1951).
6. Bevilard P.: *Mikrochemie* 39, 209 (1952).
7. Perrin D. D.: *Organicheskie Analiticheskie Reagenty*, p. 308. Mir, Moscow 1967.
8. Kotouček M., Barešová M., Nguyen Truong Son: *This Journal* 45, 3302 (1980).
9. Kotouček M., Růžička J., Vaculíková P.: *This Journal* 47, 1950 (1982).
10. Kotouček M., Bui Mai Huong: *This Journal* 42, 235 (1977).
11. Karliček R.: *This Journal* 40, 3825 (1975).
12. Yoe J. A., Jones A. L.: *Ind. Eng. Chem., Anal. Ed.* 16, 41 (1944).
13. Ketelaar J. A. A., van de Stolpe C., Goudsmit A., Dzcubas W.: *Rec. Trav. Chim. Pays-Bas* 71, 1104 (1952).

14. Kleiner K. E.: *Zh. Fiz. Khim.* **34**, 416 (1960).
15. Sommer L., Kubáň V., Havel J.: *Folia Fac. Sci. Nat. Univ. Purkyně Brno 11*, *Chemia* **7**, Op. 1 (1970).
16. Nazarenko V. A.: *Analiticheskaya Khimiya Germaniya*, p. 28. Nauka, Moscow 1973.
17. Baes Ch. F., Mesmer R. E.: *The Hydrolysis of Cations*, p. 348, 364, 365. Wiley, New York 1976.
18. Dostál V., Kotouček M., Kalašová H., Bryndová V., Šimek J.: *This Journal* **47**, 1588 (1982).
19. Bartušek M.: *Chem. Listy* **73**, 1036 (1979).
20. Bartušek M.: *Scr. Fac. Sci. Nat. Univ. Brno, Chemia* **9**, 23 (1979).
21. Kragten J.: *Talanta* **22**, 505 (1975).
22. Eckschlager K., Horsák I., Kodejš Z.: *Vyhodnocování analytických výsledků a metod*, p. 38, 83
Published by SNTL, Prague 1980.

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