

Spectrophotometric Determination of Gallium(III) with 4-(2-Pyridylazo)-resorcinol and Nitron

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Abstract. The formation and liquid-liquid extraction of ion-association complex between gallium(III) – 4-(2-pyridylazo)-resorcinol (PAR) – 1,4-diphenyl-3-(phenylamino)-1H-1,2,4-triazole (nitron, Nt), water and chloroform were studied. The optimum conditions for gallium(III) extraction as an ion-association complex, $(\text{NtH})^+[\text{Ga}^{3+}(\text{PAR})_2]^-$, were found: pH, concentration of the reagents and shaking time. The following key constants were calculated: constant of extraction ($\log K_{\text{ex}} = 6.28 \pm 0.07$), constant of association ($\log \beta = 4.98 \pm 0.05$), constant of distribution ($\log K_D = 1.30 \pm 0.02$) and recovery factor ($R/\% = 95.17 \pm 0.02$). Beer's law is obeyed for Ga(III) concentration up to $0.8 \mu\text{g cm}^{-3}$ with apparent molar absorptivity of $(10.3 \pm 0.4) \times 10^4 \text{ dm}^{-3} \text{ mol}^{-1} \text{ cm}^{-1}$ at $\lambda_{\text{max}} = 510 \text{ nm}$. Some additional characteristics, such as limit of detection ($\text{LOD} = 0.072 \mu\text{g cm}^{-3}$), limit of quantification ($\text{LOQ} = 0.24 \mu\text{g cm}^{-3}$) and Sandell's sensitivity ($\text{SS} = 0.000675 \text{ ng cm}^{-2}$) were estimated as well.

Keywords: gallium, ternary complex, solvent extraction, spectrophotometry, nitron

INTRODUCTION

Gallium is a post-transition metal of strategic importance for various priority areas of technology and science. It is known that it forms a colored anionic chelates with certain azo dyes {(4-(2-pyridylazo)-resorcinol (PAR) and 4-(2-thiazolylazo)-resorcinol (TAR)}, which are associated with bulky organic cations to form a ternary ion associated complexes. These compounds are poorly soluble in water, but readily extractable in organic solvents, and this makes it possible to apply for the purpose of extraction-spectrophotometric analysis.^{1–16} In our long term studies on ion associates a number of metals, such organic bases used are mono- and ditetrazolium salts. In this regard, studies have been conducted with the ion associates of Ga(III), which suffer the influence of the ligands, the influence of mono- and ditetrazolium bases, and of the various substituents on the molecule of the tetrazolium salt on the equilibria and the analytical characteristics of the test extraction systems. Thus, the best characteristics proved ionic associates formed between the anionic chelate of Ga(III) and PAR with the

monotetrazolium salts: 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-2H-tetrazolium bromide (thiazolyl blue tetrazolium, MTT), 3-(2-naphtyl)-2,5-diphenyl-2H-tetrazolium chloride (tetrazolium violet, TV) and 2,3,5-triphenyltetrazolium chloride (TTC).^{17–19} In this work are presented research on the extraction system Ga(III)–PAR–Nt–H₂O–CHCl₃, which tetrazolium cation is replaced with triazolium.

Nt (Figure 1) is a low-cost and low-toxic analytical reagent that has been commercially available for more than a century; however, some novel aspects of its chemical nature have been recently disclosed.¹⁵

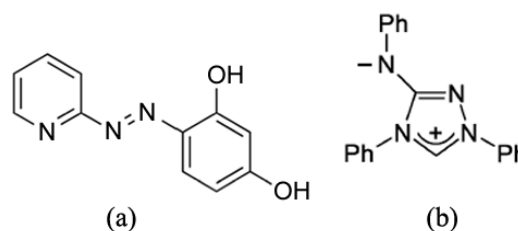


Figure 1. (a) 4-(2-Pyridylazo)-resorcinol (PAR); (b) 1,4-diphenyl-3-(phenylamino)-1H-1,2,4-triazole (nitron, Nt).

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It should be said that extraction systems containing both PAR and Nt have been weakly studied. To the best of our knowledge, the only reported investigations in this field concern vanadium(V)¹⁶ and cobalt(II)²⁰ extraction and spectrophotometric determination.

EXPERIMENTAL

The stock gallium(III) solution was prepared by heating for 20 min a known amount (0.1346 g) of Ga₂O₃ (Koch-Light Laboratories Ltd., 99,99 % in 37 % HCl (20 cm³). After cooling, the obtained clear solution was collected into a 100-cm³ calibrated flask and diluted to the mark with 6.5 mol dm⁻³ solution of HCl.¹⁸ Fresh working solutions (50 cm³) were prepared every day by mixing an aliquot of the stock solution, 0.3 cm³ of 6.5 mol dm⁻³ solution of HCl and distilled water.

PAR (Fluka AG, *p.a.*), 2.0×10⁻³ mol dm⁻³ aqueous solution.

Nitron (≥ 97 %, Fluka), 3.5×10⁻⁴ mol dm⁻³ chloroform solution.

Buffer solution, prepared by mixing 2.0 mol dm⁻³ aqueous solutions of CH₃COOH and NH₄OH.

Chloroform (additionally distilled).

WTW pH 720, Inolab.

Ultrospec 3300 pro UV / visible spectrophotometer (Amersham Biosciences), equipped with 10 mm path-length cells.

Procedure for Establishing the Optimum Operating Conditions

Aliquots of Ga(III) solution, PAR solution (up to 1.2 cm³), and buffer solution (5.0 cm³; pH ranging 3.5 to 9.3) were introduced into 250-cm³ separatory funnels. The resulting solutions were diluted with distilled water to a total volume of 10 cm³. Appropriate amounts of Nt solution and chloroform were added in a total volume of 10 cm³. Then the funnels were shaken for a fixed time (up to 5.0 min). A portion of the organic extract was filtered through a filter paper (to prevent the opportunity of water droplets transfer) into a cell and the absorbance read against a blank.

Table 1. Optimum conditions and analytical characteristics of the Ga(III)-PAR-Nt-water-chloroform system

Optimum conditions	Analytical characteristics
Wavelength – 510 nm	Molar absorptivity – $\epsilon = (10.3 \pm 0.4) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$
pH = 6.87 (acetate buffer)	Beer's law – range up to 0.8 $\mu\text{g cm}^{-3}$
$c(\text{PAR}) = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$	Limit of detection – 0.072 $\mu\text{g cm}^{-3}$
$c(\text{Nt}) = 3.0 \times 10^{-4} \text{ mol dm}^{-3}$	Limit of quantification – 0.24 $\mu\text{g cm}^{-3}$
Shaking time – 60 sec	Sandell's sensitivity – 0.000675 ng cm^{-2}

Procedure for Determination of the Distribution Constant

The distribution constant K_D was found from the ratio $K_D = A_1 / (A_3 - A_1)$, where A_1 and A_3 are the absorbances (measured against blanks) obtained after a single and triple extraction, respectively. The single extraction and the first stage of the triple extraction were performed under the optimum extraction-spectrophotometric conditions (Table 1). The organic layers were transferred into 25-cm³ calibrated flasks and the flask for the single extraction was brought to volume with Nt solution. The second stage of the triple extraction was performed by adding another 10 cm³ portion of the Nt solution to the aqueous phase, which remained after the first stage. After shaking, the organic layer was added to the one obtained after the first stage and the volume was brought to the mark with Nt solution. Before the spectrophotometric measurement, the calibrated flasks were shaken for homogenization.

RESULTS AND DISCUSSION

Absorption Spectra

Spectra of the extracted ternary Ca(III)-PAR-Nt complex and the blank are shown in Figure 2. Maxima are recorded at 510 nm, where the blank absorbs insignificantly. It is shifted to 5–6 nm as compared to the maximum of the binary Ga-PAR chelate existing in aqueous solution with similar pH ($\lambda_{\text{maxGa(III)-PAR}} = 504\text{--}505 \text{ nm}$).^{7,8}

Effect of pH

The effect of pH for the extraction of Ga with PAR and Nt is represented in Figure 3. A buffer solution with a concentration of 2.0 mol dm⁻³ (prepared by mixing 2.0 mol dm⁻³ aqueous solutions of CH₃COOH and NH₄OH) was applied to control pH. All further experiments were carried out with 5.0 cm³ buffer solution with pH 6.7–6.8.

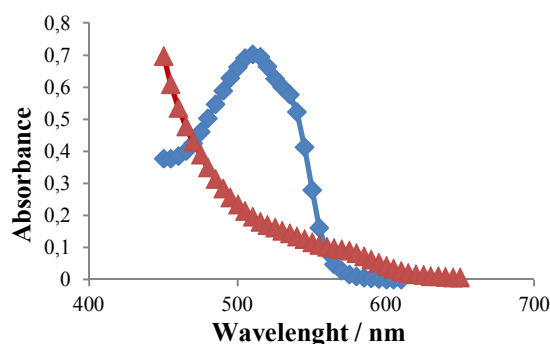


Figure 2. Absorption spectra of the ternary Ca(III)-PAR-Nt complex against blank and blank (PAR-Nt) in chloroform. $c(\text{Ga}) = 7.2 \times 10^{-6} \text{ mol dm}^{-3}$, $c(\text{PAR}) = 2 \times 10^{-4} \text{ mol dm}^{-3}$, $c(\text{Nt}) = 3.5 \times 10^{-4} \text{ mol dm}^{-3}$, pH 6.87.

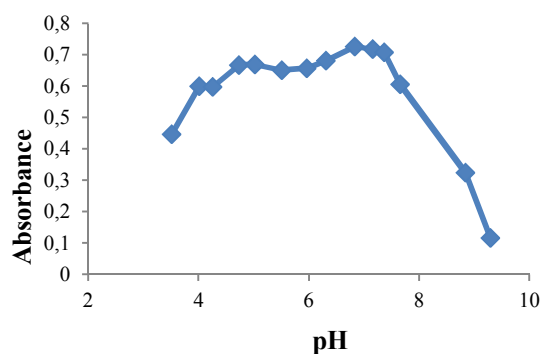


Figure 3. Absorbance of Ga-PAR-Nt complex in chloroform vs. pH of the aqueous phase plot. $c(\text{Ga}) = 7.2 \times 10^{-6} \text{ mol dm}^{-3}$, $c(\text{PAR}) = 2 \times 10^{-4} \text{ mol dm}^{-3}$, $c(\text{Nt}) = 3.5 \times 10^{-4} \text{ mol dm}^{-3}$, $\lambda = 510 \text{ nm}$, $l = 10 \text{ mm}$.

Effect of Shaking Time

The extraction equilibrium is reached for a short shaking time (about 5 seconds) (Figure 4). To guarantee complete transfer of the complex into organic phase, the authors extracted in their experiments for 60 seconds.

Effect of Reagent's Concentration

The effect of PAR and Nt concentration on the absorbance are shown in Figure 5 and Figure 6, respectively. For up to $0.8 \mu\text{g cm}^{-3}$ of Ga, the use about 1.0 cm^3 $2 \times 10^{-3} \text{ mol dm}^{-3}$ PAR (13.9-fold excess) and 7.5 cm^3 $3.5 \times 10^{-4} \text{ mol dm}^{-3}$ Nt (2.4-fold excess) was found to be sufficient for a complete gallium extraction.

Composition of the Complex and Suggested Formula

The molar PAR-to-Ga(III) and Nt-to-Ga(III) ratios were determined by the mobile equilibrium method²¹ (Figures 7 and 8), molar ratio method,²² and the method of Asmus (Figures 9 and 10).²³ The results showed that the ternary complex has a composition of 1 : 2 : 1 (Ga : PAR : Nt). We suggest the following formula of the extracted ternary species: $(\text{NtH})^+[\text{Ga}^{3+}(\text{PAR})_2]^-$.

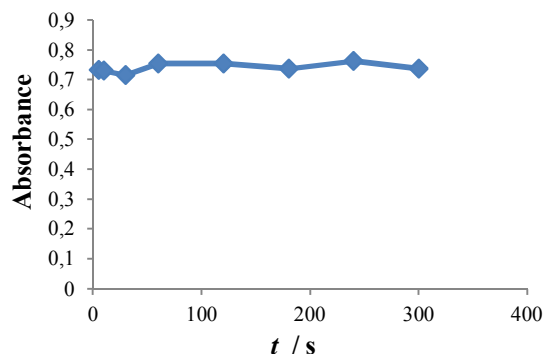


Figure 4. Absorbance of the extracted ternary Ga(III)-PAR-Nt complex vs. effect of shaking time. $c(\text{Ga}) = 7.2 \times 10^{-6} \text{ mol dm}^{-3}$, $c(\text{PAR}) = 2 \times 10^{-4} \text{ mol dm}^{-3}$, pH 6.87, $\lambda = 510 \text{ nm}$, $l = 10 \text{ mm}$.

In this formula, PAR is in deprotonated form (PAR^{2-}), while Nt is in protonated form (NtH^+).

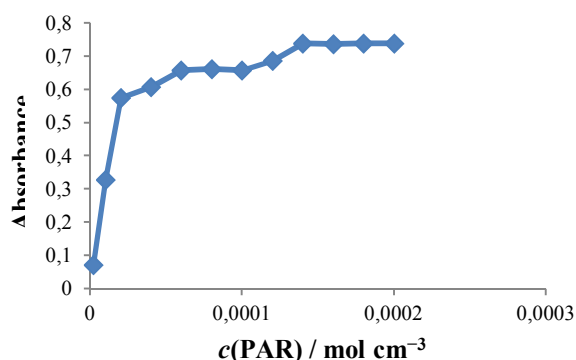


Figure 5. Absorbance of the extracted ternary Ga(III)-PAR-Nt complex vs. concentration of the PAR plots. $c(\text{Ga}) = 7.2 \times 10^{-6} \text{ mol dm}^{-3}$, $c(\text{Nt}) = 3.5 \times 10^{-4} \text{ mol dm}^{-3}$, pH 6.87, $\lambda = 510 \text{ nm}$, $l = 10 \text{ mm}$.

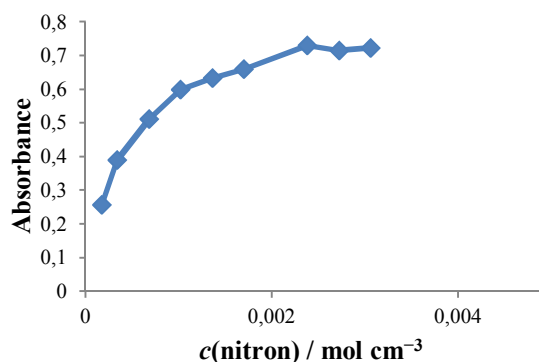


Figure 6. Absorbance of the extracted ternary Ga(III)-PAR-Nt complex vs. concentration of the Nt plots. $c(\text{Ga}) = 7.2 \times 10^{-6} \text{ mol dm}^{-3}$, $c(\text{PAR}) = 2 \times 10^{-4} \text{ mol dm}^{-3}$, pH 6.87, $\lambda = 510 \text{ nm}$, $l = 10 \text{ mm}$.

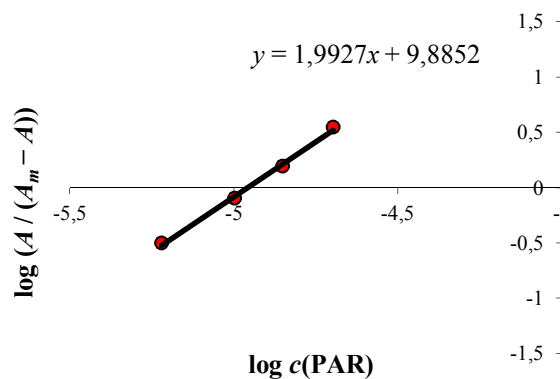


Figure 7. Determination of the PAR-to-Ga(III) molar ratio by the mobile equilibrium method. $c(\text{Ga}) = 7.2 \times 10^{-6} \text{ mol dm}^{-3}$, $c(\text{PAR}) = 2 \times 10^{-4} \text{ mol dm}^{-3}$, pH 6.87, $\lambda = 510 \text{ nm}$, $l = 10 \text{ mm}$.

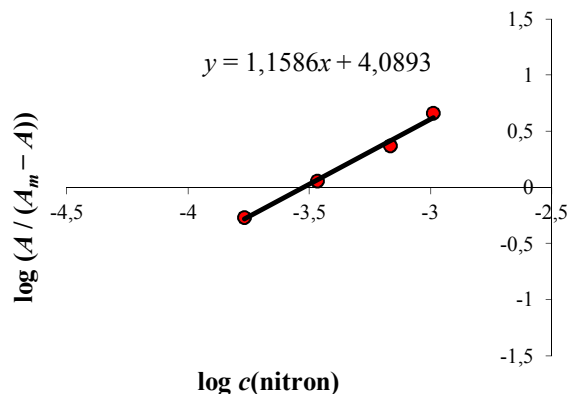


Figure 8. Determination of the Nitron-to-Ga(III) molar ratio by the mobile equilibrium method. $c(\text{Ga}) = 7.2 \times 10^{-6} \text{ mol dm}^{-3}$, $c(\text{Nt}) = 3.5 \times 10^{-4} \text{ mol dm}^{-3}$, pH 6.87, $\lambda = 510 \text{ nm}$, $l = 10 \text{ mm}$.

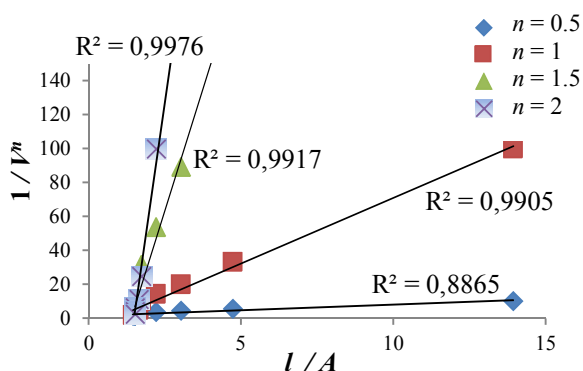


Figure 9. Determination of the Ga(III)-to-PAR molar ratios by the method of Asmus. $c(\text{Ga}) = 7.2 \times 10^{-6} \text{ mol dm}^{-3}$, $c(\text{PAR}) = 2 \times 10^{-4} \text{ mol dm}^{-3}$, pH 6.87, $\lambda = 510 \text{ nm}$, $l = 10 \text{ mm}$.

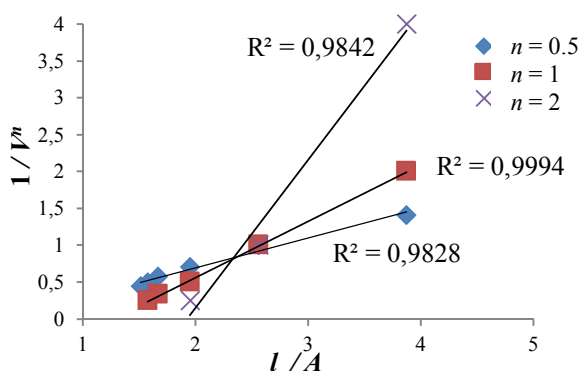


Figure 10. Determination of the Ga(III)-to-nitron molar ratios by the method of Asmus. $c(\text{Ga}) = 7.2 \times 10^{-6} \text{ mol dm}^{-3}$, $c(\text{Nt}) = 3.5 \times 10^{-4} \text{ mol dm}^{-3}$, pH 6.87, $\lambda = 510 \text{ nm}$, $l = 10 \text{ mm}$.

Equilibrium Constants and Recovery

The constant of association β were calculated by mobile equilibrium method.²¹ The constant of distribution K_D , were determined in the above described procedure. The constant of extraction (K_{ex}) and recovery factor ($R / \%$) were determined by formulae $K_{ex} = K_D \times \beta$ and $R / \% = 100 \times K_D / (K_D + 1)$, respectively. The results are present in Table 2.

Beer's Law and Analytical Characteristics

The adherence to Beer's law for Ga(III)-PAR-Nt-water-chloroform system was examined under the optimum extraction-spectrophotometric conditions (Table 1).

The linearity is observed up to $0.8 \mu\text{g cm}^{-3}$ of Ga. The molar absorptivity was calculated to be $(10.3 \pm 0.4) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. This value could compete successfully with the ones obtained for similar PAR-containing complexes (Table 3). The limit of detection (LOD) and the limit of quantification (LOQ) were estimated. Sandell's sensitivity was calculated as well (Table 1).

CONCLUSION

Gallium(III) forms chloroform extractable ternary ion-association complexes with 4-(2-Pyridylazo)-resorcinol (PAR) and 1,4-diphenyl-3-(phenylamino)-1H-1,2,4-triazole (nitron, Nt). The complex could be regarded as an ion associate between an intensively colored anion, $[\text{Ga}(\text{PAR})_2]^-$, in which gallium is +3 oxidation state, and a bulky hydrophobic cation (protonated nitron, NtH^+).

The following equilibrium constants and analytical parameters are calculated: constant of extraction ($\log K_{ex} = 6.28 \pm 0.07$), constant of association ($\log \beta = 4.98 \pm 0.05$), constant of distribution ($\log K_D = 1.30 \pm 0.02$), recovery factor ($R / \% = 95.17 \pm 0.02$), apparent molar absorptivity ($(\epsilon_{510} = (10.3 \pm 0.4) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$) for Ga(III) concentration up to $0.8 \mu\text{g cm}^{-3}$, limit of detection (LOD = $0.072 \mu\text{g cm}^{-3}$), limit of quantification (LOQ = $0.24 \mu\text{g cm}^{-3}$) and Sandell's sensitivity ($SS = 0.000675 \text{ ng cm}^{-2}$).

The calculated equilibrium constants indicate that in the aqueous phase is formed, stable enough for this type of compounds, a ternary ion - associated complex, that is very well extracted into chloroform. These features, combined with analytical parameters give rise to claims that the analysis of gallium can be performed with high sensitivity and accuracy.

Table 2. Calculated values ($P = 95 \%$) of the extraction constant (K_{ex}), distribution constant (K_D), association constant (β) and recovery factor ($R / \%$)

Extraction system	$\log \beta$	$\log K_D$	$\log K_{ex}$	$R / \%$
Ga(III)-PAR-Nt-H ₂ O-chloroform	4.98 ± 0.05	1.30 ± 0.02	6.28 ± 0.07	95.17 ± 0.02

Table 3. Spectral characteristics of some extracted in organic solvent Ga-PAR complexes

Additional reagent	Organic solvent	Molar absorptivity / dm ³ mol ⁻¹ cm ⁻¹	λ_{\max} / nm	Ref.
PAR + tetraphenylarsonium chloride	1,2-dichlorobenzene	8.20	510	[6]
PAR + pyridine + sodium acetate	isopropyl ether + butyl acetate	10.00	510	[7]
PAR + 2,3,5-triphenyltetrazolium chloride (TTC)	chloroform	9.50	510	[18]
PAR + neotetrazolium chloride (NTC)	chloroform	8.5	510	[24]
PAR + blue tetrazolium chloride (BTC)	chloroform	8.5	510	[24]
PAR + nitro blue tetrazolium chloride (NBT)	chloroform	7.1	511	[24]
PAR + tetranitro blue tetrazolium chloride (TNBT)	chloroform	6.2	513	[24]
PAR + 2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl- 2H-tetrazolium chloride (INT)	chloroform	8.2	510	[17]
PAR + tetrazolium violet (TV)	chloroform	9.6	510	[17]
PAR + thiazolil blue tetrazolium (MTT)	chloroform	9.5	515	[19]
PAR + nitron	chloroform	10.3	510	This work

The PAR and Nitron could complete successfully with many reagents for the spectrophotometric and liquid-liquid extraction for spectrophotometric determination of gallium(III).

Presented characteristics of the studied system give rise to claims that its application for the development of extraction-spectrophotometric method for determination of gallium, successfully compete described in the literature.^{17–19,24}

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