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Study on the Equilibria of the Complex Formation of the Ion-pair of Germanium(IV) with 4-Nitrocatechol and 1,4-Diphenyl-3-(phenylamino)-1*H*-1,2,4-triazole

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Abstract

The complex formation of the ion-pair formed between the anionic chelate of Ge(IV)–4-nitrocatechol (4-NC) and the cation of 1,4-diphenyl-3-(phenylamino)-1*H*-1,2,4-triazole (Nitron, Nt) in the liquid-liquid extraction system Ge(IV)–4-NC–Nt–H₂O–CHCl₃ was studied by spectrophotometry. The optimum extraction-spectrophotometric conditions for the complex formation were established. The validity of Beer's law was checked and some analytical characteristics of the system were calculated. The effect of co-existing ions and reagents on the process of complex formation was investigated. The association process in aqueous phase and the extraction equilibria were studied and quantitatively characterized. The following key constants of the processes were calculated: association constant, distribution constant, extraction constant and recovery factor. The molar ratio of the reagents was determined by independent methods. A reaction scheme and a general formula of the complex were suggested.

Keywords: Germanium(IV), nitron, ion-pair, chelate formation, extraction equilibria

1. Introduction

The germanium and its compounds are widely used in various important areas of technology, science, and medicine. Germanium is present in all living plant and animal matter in micro-trace quantities and it is essential from a biochemical point of view. The germanium is relatively less toxic compared to many other metals. The accumulation of relatively high doses of germanium (milligram order of germanium per 1 g tissue) causes severe poisoning, including impairments in kidney, nerves, muscles. On the other hand, germanium deficiency can lead to seriously hematologic disorders and tumor formation. Pharmaceutical preparations, containing germanium are effectively applied in treatment of a wide range of serious afflictions, including cancer, arthritis, osteoporosis and acute renal failure.^{1–8}

The germanium is a third row post-transition metal and its chemistry has developed considerably in the recent

years, indicated by the large number of publications in the scientific literature. Germanium(IV) forms complexes with various natural organic ligands containing O, N and S donor atoms such as polyphenols and their functional derivatives, polyhydroxycarboxylic acids, aminopolyhydroxycarboxylic acids, thiopolycarboxylic acids, 8-hydroxyquinoline and its derivatives, aromatic derivatives of hydroxyaldehydes and hydroxyketones, hydroxyazodyes. The complexes of germanium with chelate ligands containing O, N and S donor atoms have diverse industrial, biological, pharmacological and medical applications.^{9–17} Germanium(IV) gives colored chelates with aromatic compounds, containing two or more hydroxyl groups in *o*-position relative to each other. The colored anionic chelates of Ge(IV) form ion-associated complexes with bulky organic cations, like tetradecyl(trihexyl)phosphonium, methyltrioctylammonium, tetrazolium, cetylpyridinium, cetyltrimethylammonium, tetraphenylammonium, tetraphenylarsonium.^{18–25}

Nitron (Nt) (1,4-diphenyl-3-(phenylamino)-1*H*-1,2,4-triazole) is an organic compound containing a quaternary nitrogen atom included in a five-membered ring.²⁶ The structure and properties of the nitron determine its ability to form ion-associated complexes with anionic chelates of metals. The bulky hydrophobic organic substituents in the molecule of the nitron increase the extractability of the ion-associated complexes. The presence of a quaternary nitrogen atom in the molecule of the nitron determines the ability to form ionic associates with chelates of metals in aqueous phase without protonation, as opposed to the amines.^{27–30} Nitron is an important reagent for the determination of nitrates, perchlorates, borates, or traces of gold.^{31–34}

The liquid-liquid extraction is a part of the chemistry of the solutions and the coordination compounds. It is applied to study the processes of complex formation and the extraction equilibria. The extraction spectrophotometry is a relatively simple, convenient, rapid to perform and inexpensive method for preparation and characterization of new complex compounds as well as for their application in the chemical analysis.^{35–38}

The aim of this research was to study spectrophotometrically the extraction equilibria of the complex formation of the ion-pair formed between the anionic chelate of Ge(IV)–4-nitrocatechol (4-NC) and the cation of 1,4-diphenyl-3-(phenylamino)-1*H*-1,2,4-triazole (Nitron, Nt) in the liquid-liquid system Ge(IV)–4-NC–Nt–H₂O–CHCl₃ as well as to evaluate the possible applications of the system for determination of traces of germanium(IV) in alloys, biological, medical and pharmaceutical samples.

2. Experimental

2. 1. Reagents and Apparatus

GeO₂ (Sigma-Aldrich, Munich, Germany, p.a.): A 2.0×10^{-3} mol L⁻¹ aqueous solution of Ge(IV) was prepared by dissolving GeO₂ in water upon moderate heating. 4-Nitrocatechol (4-NC) (Sigma-Aldrich, p.a.): 4-NC was dissolved in distilled water to give a 1.0×10^{-2} mol L⁻¹ solution. 1,4-Diphenyl-3-(phenylamino)-1*H*-1,2,4-triazole (Nitron, Nt) (95%, Alfa Aesar GmbH & Co KG, Germany): A chloroform 3.4×10^{-4} mol L⁻¹ solution was prepared. The acidity of the aqueous medium was set using a buffer solution prepared by mixing 2.0 mol L⁻¹ aqueous solutions of CH₃COOH and NH₄OH. The organic solvent CHCl₃ was additionally distilled. The pH was checked by HI 83140 pH meter (Romania). A Camspec M508 spectrophotometer (United Kingdom), equipped with 10 mm path length cells, was employed for measurement of the absorbance.

2. 2. Procedure for Establishment of the Optimum Extraction-Spectrophotometric Conditions

The required aliquots of the solutions of Ge(IV),

4-NC and buffer needed to adjust the pH of the aqueous phase were introduced into 250 cm³ separatory funnels. The resulting solutions were diluted with distilled water to a total volume of 10 cm³. A required aliquot of a chloroform solution of Nitron was added and then the organic phase was brought up to 10 cm³ with chloroform. The funnels were shaken for a defined time. A portion of the organic extract was filtered through a filter paper into a 1 cm cell and its absorbance was measured against a blank run in parallel.

2. 3. Procedure for Determination of the Distribution Constant

The distribution constant (K_D) was determined from the ratio $K_D = A_I/(A_3 - A_I)$, where A_I and A_3 are the absorbance (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 conditions for complex formation (Table 1, column 1). The organic layers were transferred into 25 cm³ calibrated flasks and the flask from the single extraction was brought to volume with chloroform. The second stage of the triple extraction was performed by adding 7 cm³ of chloroform to the aqueous phase that remained after the first stage. After extraction, the obtained extract was added to this first stage of the triple extraction. The third stage of the triple extraction was performed in the same manner as for the second stage and the extract was added to those of the first two stages. The volume of the flask was brought to the mark with chloroform. The calibrated flasks were shaken before the spectrophotometric measurements.³⁰

3. Results and Discussion

3. 1. Optimum Extraction-Spectrophotometric Conditions

The absorption spectrum of the extract of the studied ion-pair formed between the anionic chelate of Ge(IV) with 4-NC and nitronium cation in CHCl₃ was characterized by an absorption maximum in the visible range ($\lambda_{\max} = 405$ nm) (Figure 1). The influence of the acidity of the aqueous phase on the extraction of the anionic chelate Ge(IV)–4-NC into the organic phase in the form of an ion-pair with the nitronium cation was investigated. The maximum and constant extraction of the ion-associated complex is achieved in the pH range from 3.0 to 4.5. Acetate buffer solution with pH = 4.0 was used in all further experiments. The results showed that the extraction equilibrium is achieved for shaking time of not less than 60 s. A longer shaking time did not affect the absorbance. The experiments were performed for 2 min. The concentrations of the reagents are the most important factor inf-

Figure 1. Absorption spectra of the complex Ge(IV)–4-NC–Nt and of the blank sample 4-NC–Nt in CHCl_3 . $C_{\text{Ge(IV)}} = 2.0 \times 10^{-5} \text{ mol L}^{-1}$; $C_{4\text{-NC}} = 5.0 \times 10^{-4} \text{ mol L}^{-1}$; $C_{\text{Nt}} = 1.7 \times 10^{-4} \text{ mol L}^{-1}$; pH = 4.0; $\lambda = 405 \text{ nm}$; $\tau = 2 \text{ min}$

luencing the extraction equilibria. The chelate formation of Ge(IV)–4-NC requires 15.0-fold excess of 4-NC ($C_{4\text{-NC}} \geq 3.0 \times 10^{-4} \text{ mol L}^{-1}$) and 5.1-fold excess of Nitron ($C_{\text{Nt}} \geq 1.0 \times 10^{-4} \text{ mol L}^{-1}$) for maximum association and extraction. The optimum experimental conditions for the extraction of the ion-associated complex are summarized in Table 1, column 1.

3. 2. Beer's Law, Apparent Molar Absorptivity and Other Analytical Characteristics

The range of obedience to Beer's law, i.e. the linear relationship between the germanium(IV) concentration in the aqueous phase ($C_{\text{Ge(IV)}}$, $\mu\text{g mL}^{-1}$) and the absorbance of the ion-association complex in the organic phase after extraction was studied using regression analysis under the optimum conditions for complex formation. The equation of a straight line was found to be $Y = 0.3807 X + 0.0483$ with a correlation coefficient squared 0.9982. Under the optimum conditions for complex formation, the linearity

is observed for concentrations up to $5.81 \mu\text{g cm}^{-3}$ Ge(IV). Further analytical characteristics, such as apparent molar absorptivity ϵ' , adherence to Beer's law, Sandell's sensitivity, limit of detection and limit of quantification, are shown in Table 1, column 2.

3. 3. Effect of Co-existing Ions and Reagents on the Complex Formation

The effect of various co-existing ions and reagents on the process of complex formation of the ion-pair formed between the anionic chelate Ge(IV)–4-NC and nitronium cation was studied under optimum extraction conditions (Table 1, column 1). The concentration of Ge(IV) in the presence of the co-existing ions and reagents was determined from the sequence of Beer's law. A deviation of $\pm 3\%$ from the absorbance of the ion-associate in the absence of co-existing ions was accepted as an interfering effect. The results are presented in Table 2. From them, it can be concluded that most of the ions studied do not interfere, but some of them, like Br^- , F^- , I^- , $\text{C}_6\text{H}_5\text{O}_7^{2-}$, NO_3^- , $\text{C}_2\text{O}_4^{2-}$ and complexone III in concentrations higher than the indicated ones, hinder the extraction of Ge(IV) as an associated complex with 4-NC and Nitron. The extraction equilibrium is hindered by Al(III), Cr(III), Cr(VI), Fe(III), Mo(VI), W(VI) and V(V). The interfering ions can be masked or removed from the extraction system to avoid this. Our investigations as well as the studies published in the literature show that the some of the co-existing ions, like Al(III), Cr(III) and Fe(III) can be removed by their pre-precipitation with OH at pH = 11. The co-existing ions, like Mo(VI) and W(VI) can be masked with added L-ascorbic acid, Complexone III, $\text{C}_6\text{H}_5\text{O}_7^{2-}$ or $\text{C}_2\text{O}_4^{2-}$ in concentrations lower than the indicated.³⁹ Vanadium(V) can be co-precipitated with Fe(III) in alkali medium.⁴⁰

3. 4. Molar Ratios of the Complex, Reaction Scheme and Suggested General Formula

The molar ratios of the complex were determined by three independent methods. The straight-line method of

Table 1. Optimum extraction-spectrophotometric conditions and analytical characteristics of the system Ge(IV)–4-NC–Nt– H_2O – CHCl_3

Optimum Conditions	Analytical Characteristic
Absorption maximum (λ_{max}) 405 nm	Apparent molar absorptivity (ϵ')
$(2.98 \pm 0.11) \times 10^4 \text{ L mol}^{-1} \text{cm}^{-1}$	
Volume of the aqueous phase 10 cm^3	True molar absorptivity (ϵ)
$(3.09 \pm 0.25) \times 10^4 \text{ L mol}^{-1} \text{cm}^{-1}$	
Volume of the organic phase 10 cm^3	Sandell's sensitivity (SS) 2.43 ng cm^{-2}
pH of the aqueous phase 3.0–4.5	Adherence to Beer's law
up to $5.81 \mu\text{g cm}^{-3}$	
Shaking time (τ) 2 min	Relative standard deviation (RSD) 1.01%
Concentration of 4-NC $\geq 3.0 \times 10^{-4} \text{ mol L}^{-1}$	Limit of detection (LOD) 0.34 $\mu\text{g cm}^{-3}$
Concentration of Nt $\geq 1.0 \times 10^{-4} \text{ mol L}^{-1}$	Limit of quantification (LOQ) 1.13 $\mu\text{g cm}^{-3}$

Table 2. Effect of co-existing ions and reagents on the complex formation of the ion-associate Ge(IV)–4-NC–Nt for extraction in the presence of 14 µg Ge(IV)

Co-existing ion and reagent	Co-existing ion and reagent, µg/10 cm ³ aqueous phase	Ge(IV) found, µg	R, %
Na ⁺	10000	14.30	102.14
K ⁺	10000	13.75	98.21
Cu ²⁺	10000	14.23	101.64
Zn ²⁺	10000	14.38	102.71
Cd ²⁺	10000	13.92	99.43
Ni ²⁺	10000	14.09	100.64
Mn ²⁺	10000	14.19	101.36
Co ²⁺	10000	13.66	97.57
Al ³⁺	20		interference
Cr ³⁺	20		interference
Fe ³⁺	20		interference
V(V)	10		interference
Cr(VI)	30		interference
W(VI)	20		interference
Mo(VI)	30		interference
F ⁻	100	14.31	102.21
Cl ⁻	10000	14.18	101.29
Br ⁻	3500	14.39	102.79
I ⁻	5000	14.26	101.86
NO ₃ ⁻	2500	13.83	98.79
PO ₄ ³⁻	10000	13.97	99.79
C ₂ O ₄ ²⁻	500	14.37	102.64
C ₆ H ₅ O ₇ ³⁻	400	13.72	98.00
Complexone ²²²	3000	14.38	102.71
L- Ascorbic acid	10000	13.80	98.57

Figure 2. Determination of the molar ratio (n) Ge(IV):4-NC by the method of Asmus. $C_{\text{Ge(IV)}} = 2.0 \times 10^{-5} \text{ mol L}^{-1}$; $C_{\text{Nt}} = 1.7 \times 10^{-4} \text{ mol L}^{-1}$; pH = 4.0; $\lambda = 405 \text{ nm}$; $\tau = 2 \text{ min}$

Asmus and the mobile equilibrium method were applied to prove the molar ratios Ge(IV):4-NC and Ge(IV):Nt.⁴¹ The results from the application of these methods are shown in Figures 2–4, respectively. On the basis of the results it can be concluded that Ge(IV), 4-NC and Nitron in-

Figure 3. Determination of the molar ratio (n) Ge(IV):Nt by the method of Asmus. $C_{\text{Ge(IV)}} = 2.0 \times 10^{-5} \text{ mol L}^{-1}$; $C_{\text{4-NC}} = 5.0 \times 10^{-4} \text{ mol L}^{-1}$; pH = 4.0; $\lambda = 405 \text{ nm}$; $\tau = 2 \text{ min}$

teract in molar ratio 1:3:2. The application of the method of continuous variations confirmed the molar ratio Ge(IV):Nt = 1:2 (Figure 5).⁴¹

Figure 4. Straight lines by the mobile equilibrium method for determination of the molar ratios Ge(IV):4-NC and Ge(IV):Nt; $C_{\text{Ge(IV)}} = 2.0 \times 10^{-5} \text{ mol L}^{-1}$; pH = 4.0; $\lambda = 405 \text{ nm}$; $\tau = 2 \text{ min}$ ▲ Ge(IV) : 4-NC, $C_{\text{Nt}} = 1.7 \times 10^{-4} \text{ mol L}^{-1}$; ● Ge(IV) : Nt, $C_{4\text{-NC}} = 5.0 \times 10^{-4} \text{ mol L}^{-1}$

Figure 5. Determination of the molar ratio (n) Ge(IV):Nt by the method of continuous variations. $C_{\text{Ge(IV)}} + C_{\text{Nt}} = 1.0 \times 10^{-3} \text{ mol L}^{-1}$; $C_{4\text{-NC}} = 5.0 \times 10^{-4} \text{ mol L}^{-1}$; pH = 4.0; $\lambda = 405 \text{ nm}$; $\tau = 2 \text{ min}$

Germanates containing $[\text{Ge}(\text{OH})_6]^{2-}$ ions are already described in the literature although in dilute aqueous solutions the major determinate ions appear to be $[\text{GeO}(\text{OH})_3]^-$, $[\text{GeO}_2(\text{OH})_2]^{2-}$ and $\{[\text{Ge}(\text{OH})_4]_8(\text{OH})_3\}^{3-}$.⁹ The carried out experiments showed that the complex formation and the extraction of the ion-associated complex have occurred in dilute solutions and the molar ratio establis-

hed by the independent methods mentioned above was Ge(IV):4-NC:Nt = 1:3:2. Therefore, the complex formation of anionic chelate Ge(IV)–4-NC can be given by equation (1):

Having in mind the reaction of chelate formation of Ge(IV)–4-NC and molar ratio indicated above, it can be suggested that the formation of the ion-associate in the aqueous phase, its distribution between the aqueous and the organic phases and its extraction in chloroform can be given by the following equations (2–4).

Hence, the ion-pair formed between the anionic chelate of Ge(IV)–4-NC and the nitronium cation can be represented by the general formula $(\text{Nt})_2\{\text{Ge}[\text{O}_2\text{C}_6\text{H}_3(\text{NO}_2)]_3\}$.

3. 5. Extraction Equilibria, True Molar Absorptivity and Recovery Factor

The association process in aqueous phase and the extraction equilibria were investigated and quantitatively characterized with respect to the following key constants: association constant, distribution constant, extraction constant and recovery factor.

The association constant β was determined by the method of Komar-Tolmachev from equation (5).⁴¹

$$\beta = (1/n)^n / [\varepsilon (\text{tg } \alpha)^{n+1}] \quad (5)$$

where l is the cuvette thickness ($l = 1 \text{ cm}$); n is the molar ratio between the components independently determined (e.g. by the mobile equilibrium method, the straight-line method of Asmus or the method of continuous variations) ($n = 2$), ε is the true molar absorptivity.

The true molar absorptivity ε was determined by the method of Komar-Tolmachev (Figure 6) from the equation of a straight line $Y = 2.1644 X + 3.2386$ ($\varepsilon = 1 / (b \times 10^{-5})$) and its value is given in Table 1, column 2.⁴¹

The distribution constant (K_D) was determined by equation (6), where A_1 and A_3 are the absorbance (measured against blanks) obtained after a single and triple extraction, respectively.

Figure 6. Dependency of $(C//A)$ on $A^{-n/(n+1)}$ (method of Komar-Tolmachev). $C = C_{\text{Ge(IV)}} \text{ mol L}^{-1}$; $C_{\text{Nt}} = 2 C_{\text{Ge(IV)}} \text{ mol L}^{-1}$; $C_{4\text{-NC}} = 5.0 \times 10^{-4} \text{ mol L}^{-1}$; A – absorbance; l – cell thickness, $l = 1 \text{ cm}$; $n = 2$

$$K_D = \{(\text{Nt})_2\{\text{Ge}[\text{O}_2\text{C}_6\text{H}_3(\text{NO}_2)_3]\}\}(\text{org}) / \{(\text{Nt})_2\{\text{Ge}[\text{O}_2\text{C}_6\text{H}_3(\text{NO}_2)_3]\}\}(\text{aq}) (A_I / (A_3 - A_I)) \quad (6)$$

The recovery factor was determined from the equation (7):

$$R\% = 100 K_D / (K_D + 1) \quad (7)$$

The extraction constant K_{ex} was calculated by two independent methods:

$$(i) \log K_{\text{ex}} = \log K_D + \log \beta \quad (8)$$

where β was determined by the method of Komar-Tolmachev.

(ii) the method of Likussar-Boltz:⁴²

The method of Likussar-Boltz uses the data from the method of continuous variations (Figure 5). The extraction constant K_{ex} was calculated by the equation of Likussar-Boltz for molar ratio 1:2 (equation 9):

$$\log K_{\text{ex}} = 0,3522 - 2 \log K + \log Y_{\text{max}} - 3 \log (1 - Y_{\text{max}}) \quad (9)$$

where K is the total concentration of reagents ($K = C_{\text{Ge(IV)}} + C_{\text{Nt}} = 1.0 \times 10^{-3} \text{ mol L}^{-1}$); Y_{max} and $(1 - Y_{\text{max}})$ are determined from the additionally plotted normalized absorbance curve ($Y_{\text{max}} = 0.933$; $(1 - Y_{\text{max}}) = 0.067$).

The values of the equilibrium constants and the recovery factor are presented in Table 3. The results obtained by independent methods are statistically dissimilar and confirm the proposed scheme of the process of complex formation of the ion-pair in the aqueous phase, its distribution between the aqueous and the organic phases and its extraction in chloroform.

4. Conclusion

The extraction equilibria for complex formation of the ion-pair formed between the anionic chelate of Ge(IV)–4-nitrocatechol (4-NC) and the cation of 1,4-diphenyl-3-(phenylamino)-1*H*-1,2,4-triazole (Nitron, Nt) was studied by spectrophotometry. The processes of the chelate formation and extraction of the ion-associated complex Ge(IV)–4-NC–Nt into chloroform were investigated. The optimum conditions for the association in aqueous phase and extraction of the ion-associated complex were established. The validity of Beer's law was checked and a linear relationship between the germanium(IV) concentration in the aqueous phase and the absorbance of the ion-association complex in the organic phase extraction was observed for concentrations up to $5.81 \mu\text{g mL}^{-1}$ Ge(IV). The presence of hydrophobic substituents, phenyl groups in the molecule of the triazole, increased the solu-

Table 3. Values of the Equilibrium Constants and the Recovery Factor

Equilibrium Constant and Recovery Factor	Value
Equilibrium (equation 3) - Association constant β	
$\beta = (\text{Nt})_2\{\text{Ge}[\text{O}_2\text{C}_6\text{H}_3(\text{NO}_2)_3]\}(\text{aq}) / \{[(\text{Nt})^+]^2(\text{aq})\{\{\text{Ge}[\text{O}_2\text{C}_6\text{H}_3(\text{NO}_2)_3]\}^2(\text{aq})\}\}$	$\log \beta = (8.90 \pm 0.75)^a$ $\log \beta = (9.47 \pm 0.21)^b$
Equilibrium (equation 4) – Distribution constant K_D	
$K_D = \{(\text{Nt})_2\{\text{Ge}[\text{O}_2\text{C}_6\text{H}_3(\text{NO}_2)_3]\}\}(\text{org}) / \{(\text{Nt})_2\{\text{Ge}[\text{O}_2\text{C}_6\text{H}_3(\text{NO}_2)_3]\}\}(\text{aq})$	$\log K_D = (1.30 \pm 0.01)^c$
Equilibrium (equation 5) - Extraction constant K_{ex}	
$K_{\text{ex}} = \{(\text{Nt})_2\{\text{Ge}[\text{O}_2\text{C}_6\text{H}_3(\text{NO}_2)_3]\}\}(\text{org}) / \{[(\text{Nt})^+]^2(\text{aq})\{\{\text{Ge}[\text{O}_2\text{C}_6\text{H}_3(\text{NO}_2)_3]\}^2(\text{aq})\}\}$	$\log K_{\text{ex}} = (10.20 \pm 0.76)^d$ $\log K_{\text{ex}} = (9.85 \pm 0.45)^e$
Recovery factor $R\%$	$R = (95.21 \pm 0.03)\%^f$

^a Calculated by Komar-Tolmachev method (equation (6)); ^b Calculated by Holme-Langmyhr method;⁴² ^c Calculated by equation (6); ^d Calculated by equation (8), where β is determined by the Komar-Tolmachev method; ^e Calculated by Likussar-Boltz method (equation (9)); ^f Calculated by equation (7).

bility of the ion-associated complex in the organic solvent. The molar ratio of the components, determined by independent methods, shows that the ion-associated complex could be represented with the general formula $(\text{Nt})_2\{\text{Ge}[\text{O}_2\text{C}_6\text{H}_3(\text{NO}_2)_3]\}_3$. A corresponding reaction scheme of the complex was also suggested. The equilibrium constants and analytical characteristics needed for the quantitative assessment of the extraction equilibrium were calculated, i.e. the association constant (β), the distribution constant (K_D), the extraction constant (K_{ex}), the recovery factor (R), the apparent molar absorptivity (ϵ'), the true molar absorptivity (ϵ), the limit of detection (LOD), the limit of quantification (LOQ) and the Sandell's sensitivity (SS). From the analytical characteristics of the extraction system $\text{Ge(IV)}-4\text{-NC-Nt-H}_2\text{O-CHCl}_3$, it can be concluded that the ion-pair formed between the anionic chelate of $\text{Ge(IV)}-4\text{-NC}$ and the nitronium cation allows determinations of Ge(IV) with a high sensitivity.

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Povzetek

S pomočjo spektrofotometrije smo proučili tvorbo komplekso med anionskim kelatnim kompleksom Ge(IV)–4-nitroka-tehol (4-NC) in kationom 1,4-difenil-3-(fenilamino)-1*H*-1,2,4-triazolom (Nitron, Nt) v tekočina-tekočina ekstrakcijskem sistemu Ge(IV)–4-NC–Nt–H₂O–CHCl₃. Določili smo optimalne ekstrakcijsko-spektrofotometrične pogoje za tvorbo kompleksov. Preverjena je bila veljavnost Beerovega zakona ter izračunane nekatere analzne karakteristike. Določen je bil tudi vpliv različnih ionov in reagentov na proces tvorbe kompleksov. Asociacijski proces v vodni fazi in ekstrakcijsko ravnotežje je bilo proučeno in kvantitativno okarakterizirano. Sledeče najpomembnejše konstante procesov so bile izračunane: asociacijska konstanta, distribucijska konstanta, ekstrakcijska konstanta in izkoristek ekstrakcije. Z neodvisnimi metodami smo določili molske deleže. Predlagana je reakcijska shema, splošna formula in struktura kompleksa.