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3-Phenyl-2, 4-tiazolidindion as an analytical reagent for extraction-photometric determination of nickel (II)

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Abstract
The possibility of using 3-phenyl-2,4-*thiazolidinedione* (L) for the photometric determination of nickel (II) has been studied. Dichloroethane, chloroform and carbon tetrachloride were the best extractants. With a single extraction with chloroform, 97.3% of nickel is recovered as a complex. The complex of nickel (II) is extracted into chloroform in the range of pH 4.2-6.0. The maximum analytical signal in the complexation of nickel with L is observed at 492 nm. The molar absorption coefficient is 2.65×10^4. The ratio of components in the complex is Ni: L = 1: 2. The extract of the nickel complex obeys the basic law of absorption at a concentration of 0.5-15 μg / ml. Based on the results of spectrophotometric studies of nickel (II) with L, methods for determining nickel in various objects have been developed.

Keywords: Nickel, 3-phenyl-2, 4-thiazolidinedione, extraction-photometric method

1. Introduction

Nickel is one of the common components that are constantly present in natural waters. Nickel can get into the water from the soil, as well as as a result of decomposition of plant and animal organisms present in water bodies. Nickel compounds are transferred to tanks with wastewater from nickel workshops, synthetic rubber plants and nickel plants. In rivers of unpolluted and slightly polluted waters, nickel concentrations usually range from 0.8 to 10 μg / l, in polluted waters - several tens of micrograms per liter.

Nickel compounds play an important role in the formation of blood, are oxidative catalysts in the form of organometallic complexes in animals and humans. Increased nickel content has a specific effect on the vascular endothelium (especially the brain and adrenal glands), where multiple hemorrhages occur.

Industrial and waste waters of many industrial enterprises contain high concentrations of heavy and non-ferrous metals, including nickel (II), therefore the determination of nickel content in industrial waters is an actual problem.

Atomic absorption spectrometry of a flame and graphite furnace and spectrophotometric methods provide accurate and rapid determination of nickel in natural and waste waters [1]. However, very often a direct definition cannot be used, since a low concentration of the analyzed or matrix noise.

The most widely used methods for separation and pre-concentration of nickel are liquid-liquid extraction [2], precipitation [3] and chelate resin [4]. Many classical ligands, such as Dimethylglyoxime, Dithizone and sodium Diethyldithiocarbamate, are known as the definition of an extraction / spectrophotometric extractant of nickel [5].

Oxyphenolate and hydroxythiophenol nickel complexes are insoluble in chloroform, whereas complexes of a mixed ligand with hydrophobic amines and 4-aminophenols dissolve easily in various organic solvents [6–8].

We have studied the possibility of using 3-phenyl-2, 4-thiazolidinedione (PhTAD, L) for photometric determination of nickel (II).

2. Experimental
2.1 Reagents and Apparatus

Nickel stock solution (1mg/ml) was prepared by dissolving an appropriate amount of Ni (NO₃)₂×6H₂O in 1 ml of nitric acid in a 100 ml volumetric flask and diluted to the mark with water.

Nickel standard solutions were prepared by appropriate dilution of the stock solution [9]. The stock solution of various metal ions and anions were prepared by dissolving the appropriate metal salts in distilled water or with suitable dilute acids and making up to a known volume.

Solutions of L in chloroform (0.01M) were used. As an estrogen the cleared chloroform was applied.

The ionic force of solutions was supported a constant ($\mu = 0.1$) introduction of the calculated quantity of KCl. To create the necessary acidity of the solutions used acetate buffer solution.

The absorbance of the extracts was measured using a KFK-2 photocolorimeter and an SF-26 spectrophotometer; the equilibrium value of the pH of aqueous phase was measured using a I-120.2 potentiometer with a glass electrode. IR - spectra were recorded on a spectrophotometer UR-20. All measurements was carried out at 20 ± 5° C.

2.2 General Procedure
2.2.1 General Procedure for the Determination of nickel (I)
Portions of stock solutions of nickel (II) varying from 0.1 to 1.0 mL with a 0.1 mL step, a 2.2 mL portion of a 0.01 M solution of L were placed in to calibrated test tubes with groundglass stoppers (the volume of the organic phase was 5 mL). The required value of pH was adjusted by adding $CH_3COOH + CH_3COONH_4$ buffer solutions (pH 2-10). The volume of the aqueous phase was increased to 20 mL using distilled water. In 6 minnute after the complete separation of the phases, the organic phase was separated from the aqueous phase and the absorbance of the extracts was measured on KFK-2 at room temperature and 490 nm (ℓ=0.5cm).

2.2.2 Determination of nickel (II) in tap water
Pour 2 liters of water into a flask and evaporate to dryness. The dry residue is dissolved in a buffer solution of pH 4 and transferred to a 50 ml flask by filtration. In an aliquot (3 ml), photometric determination of nickel.

3. Results and Discussion
The reagent solution in chloroform has a yellowish color. The maximum light absorption is observed at 370 nm. Structure of ligand was confirmed by using IR spectra [10].
IR (KBr cm^{-1}): 3210 cm^{-1} (NH), 1650, 1725 cm^{-1} (C=O), 1254cm^{-1} (C-N), 1495 cm^{-1} (-CH$_2$), 2345(C-S), 1612(C=C Ar), 1570 cm^{-1} (C$_6$H$_5$). The chemical structure of the reagent is shown in Fig.1.
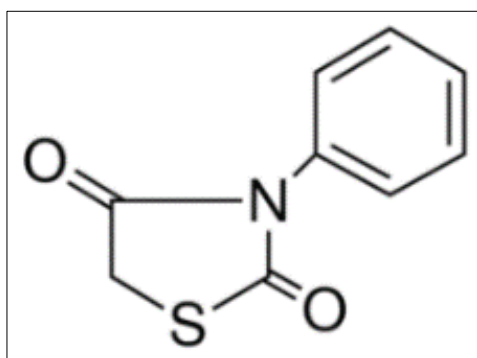

Fig 1: The chemical structure of PhTAD

Ni(II) reacts with PhTAD and gives a blue colored complexes. These complexes are soluble in non-polar solvents.

3.1 Choice of organic solvent.
$CHCl_3$, CCl_4, $C_2H_4Cl_2$, C_6H_6, $C_6H_5CH_3$, $C_6H_4(CH_3)_2$, iso-butanol, iso-pentanol, n-hexanol, and their mixtures were tested as extractants. $CHCl_3$ demonstrated the best result; it was used in further experiments. At the optimum conditions this solvent provides degrees of extraction R=97.3 %. The concentration of nikel in the organic phase was determined with Dimethylglyoxime [5] by photometric measurements after back extraction, while in the aqueous phase it was determined by the difference.

3.2 Effect of pH
The change in pH affected the Ni (II) complexation - PhTAD. Therefore, the absorption of the complex was studied between pH 2.8 to 9.3, using acetate buffer solution. The absorbance values of the extracted complex were measured. The maximum absorbent was obtained in the pH range from 4.2 to 6.0 (Figure 2). In addition to this pH range, the observed absorption values were lower. Thus, further extraction and determination was carried out on 5.0.
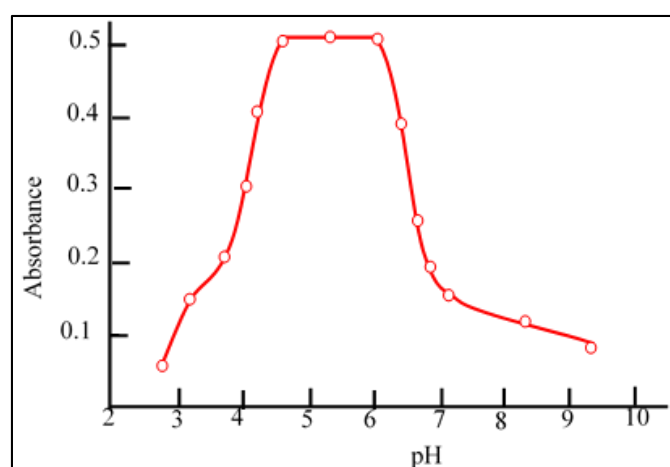

Fig 2: The dependence of the optical density of the complex on the pH of the aqueous phase. $C_{Ni (II)} = 2.035\times10^{-5}$ M; C $_{PhTAD}$ =5.0×10^{-4}M, КФК-2, λ=490 nm, l=1.0 см.

3.3 Electronic absorption spectra
PhTAD forms a poorly soluble complex with nickel (II). The complex can be easily extracted quantitatively in chloroform in the range of pH 4.0-5.9 the maximum absorption in the visible region at 495 nm (Figure 3). The molar absorption coefficient of light is 2.65×10^4 L mol^{-1} cm^{-1}.

## 3.4 The effect of reagent concentration and shaking time
For the formation and extraction of the complex, a 11–14-fold excess of the complexing agent is required; for example, the optimal conditions for the formation and extraction of these compounds are provided by 5.0×10^{-4} M Ph. TAD. However, it was found that the presence of an excess of the reagent solution does not affect the absorption of the color reaction. Under optimal conditions, the absorption of the complex formed in the aqueous phase after equilibration with chloroform initially increased, and then reached a constant and maximum value within 60-300 s. Therefore, as the optimal equilibration time for each extraction, 90 s were chosen during further studies and were used in the proposed procedure. The color stability of the Ni (II)-Ph TAD complex over time shows that absorption due to the species selected is stable up to 36 hours of which there is a slight decrease in absorption.
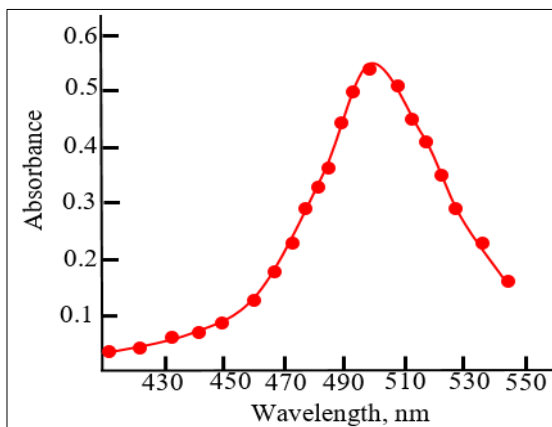
Fig 3: Absorption of complex Ni – Ph TA, $C_{Ni (II)} = 2.035 \times 10^{-5}$ M; C
Ph TAD $=5.0 \times 10^{-4}$M, SF-26, l=1.0 см

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3.5 Composition, structure and stability

The molar ratios between the components of the complex were found by several methods: Starik–Barbanel relative yield method, straight line method and equilibrium shift method (Figure 4). The results suggest the complex composition of 1:2 (Ni: PhTAD). Additional experiments by the Akhmedly's method [12] showed that the complex exists in monomeric form in the organic phase (the obtained coefficient of polymerization γ was equal to 1.02).
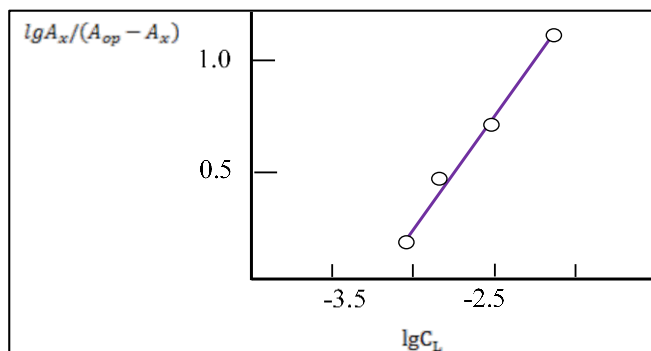

Fig 4: Determination of the ratio of components by equilibrium shift method for Ni –Ph TAD. $C_{Ni} = 2.035 \times 10^{-5}$ M; $C_L = 5.0 \times 10^{-4}$M, pH 5, λ=590 nm, KFK-2, ℓ=1.0 sm.

The stability constant of the Ni(II) -PhTAD complex was determined and lgβ = 14.96 was found at room temperature. Using the Nazarenko method, it was found that Ni (II) in the complexes is present as Ni $^{2+}$. The number of protons substituted by cobalt in one PhTAD molecule turned out to be equal [13].
New bands were observed in the region of 410-590 cm^{-1} in the complex, which were absent in the spectrum of the ligand. The bands between 457 cm $^{-1}$ were assigned to stretching frequencies ν (Ni – O), and the band between 578 cm^{-1} was

assigned to stretching frequencies ν (Ni –S), respectively. Proceeding from the obtained data, we propose the following structure for the extracted complex (Figure 5).
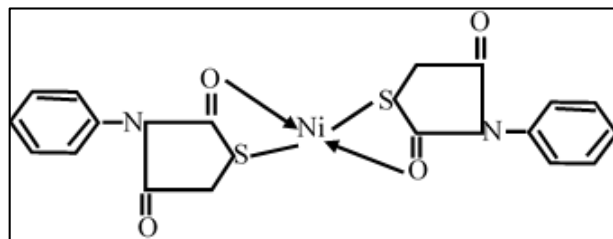
Fig 5: Suggested structure of the complex

Table 1: Optical characteristics, precision and accuracy of the spectrophotometric determination of Ni(II) with PhTAD.

Parameter	Value
Color	red
The pH range of education and extraction	2.8-9.3
The pH range of maximum extraction	4.2-6.0
λ_{max} (nm)	492
Molar absorptivity (L· mol^{-1} cm^{-1})	$2.65 \cdot 10^4$
Sandell's sensitivity (ng·cm^{-2})	2.19
R,%	97.3
The equation of calibration curves	0.025+0.0385x
Correlation coefficient	0.9963
lg k$_e$	5.75
Stability constant (β)	14.96
Beer's law range (µg·mL^{-1})	0.5-15
Limit of detection (LOD): ng ·mL	13
Limit of quantification (LOQ): ng ·mL^{-1}	45

A thermogravimetric study of the Ni-PhTAD complex showed that the thermal decomposition of the complex occurs in two stages: at 50–120°C, water evaporates at 440–510°C-decomposable PhTAD. The end product of thermolysis of the complex is NiO.
The dimensions of the equilibrium constant K$_e$, calculated by the formula lgK$_e$ = lgD - lg [L], are presented in table 1. In conclusion, the analytical parameters related to the proposed method are given in table 1.

3.6 Effect of the foreign ions

To evaluate the complex applicability for photometric determination of nickel, we examined the influence of foreign ions and reagents. The results showed that great excesses of alkali, alkali earth, and rare earth elements, as well as F⁻, Cl⁻, Br⁻, SO_3^{2-}, SO_4^{2-} and $C_2O_4^{2-}$ do not interfere with determination. The influence of Fe(III) was eliminated by thioglycolic acid; Ti(VI), by ascorbic acid; Cu(II), by thiourea; and Mo(VI) and Nb(V), by oxalate (Table 2). If a 0.01 mol L⁻¹ solution of EDTA was used, Ti(IV), V(IV), Nb(V), Ta(V), Mo(VI) and Fe(III) exhibited no interference.

Table 2: Influence of interfering ions on the determination of nickel (II) with (30.0 µg Ni added)

İon	Molar Excess of the Ion	Masking agent	Found Ni, µg	RSD (%)
Ti (IV)	50	Ascorbic acid	29.9	4
Fe (II)	80		29.9	4
Fe (III)	65	Ascorbic acid	30.0	5
Cd (II)	120		30.2	3
Al (III)	170		29.8	3
Co (II)	30	EDTA	30.2	5
Hg (II)	40		30.3	4
Zr (IV)	70		29.7	3
Cu (II)	30	Thiourea	29.9	5
Zn (II)	45		29.5	4

UO_2^{2+}	55		30.0	4
Ag (I)	40		30.2	5
Ta (V)	60	Ascorbic acid	29.9	4
V (IV)	20		29.8	3
Mo (VI)	40	EDTA	30.3	5
W (VI)	59		29.9	3
Cr (III)	120		29.9	3
Nb (V)	40	$C_2O_4^{2-}$	30.5	6
Fluoride	60		30.6	4
H_3PO_4	50		30.3	3
Salicylic acid	20		30.0	3
Sulfosalicylic acid	40		29.5	6
Ascorbic acid	20		30.1	5
Tartaric asid	20		30.5	5
Oxalate	40		30.8	4

3.7 Calibration graph and analytical characteristics

The nickel (II) extracts conform to the Beer's law in the range of 0.5-15 µg mL^{-1} with a correlation coefficient of 0.9963 (8 standards used). The limit of detection, calculated according to Aleksovskii *et al.* [14] was 13 ng mL^{-1}. The straight-line equation was $y=0.025+0.0385x$, where y is the absorbance and x is the Ni (II) concentration in µg mL^{-1}. The corresponding molar absorptivity was λ = 492 nm, ε = 2.65×10^4 L mol^{-1} cm^{-1}; it is higher than the molar absorptivity's reported for similar liquid-liquid extraction-spectrophotometric procedures involving pyridoxal-4-phenyl-3-thiosemicarbazone (λ=430 nm, ε=1.92×10^4 L mol^{-1} cm^{-1}) [15], N-ethyl-3-carbazo-lecarboxaldehyde-3-thiosemicarbazone (λ=400 nm, ε=1.114× 10^4 L mol^{-1} cm^{-1}) [16], α- furildioxime (λ = 435 nm, ε = 2.0×10^4 L mol^{-1} cm^{-1}) [5], sodium isoamyl xantene (λ=360 nm, ε = 1.20×10^4 L mol^{-1} cm^{-1})[17], 1-hydroxy-2-acetonaphtoneoxime (λ = 396 nm, ε = 5.7×10^3 L mol^{-1} cm^{-1}) [18], 2-hydroxy-1-naphthaldoxime (λ=396 nm, ε=8.1×10^3 L mol^{-1} cm^{-1}) [19], dimethylglyoxime (λ=380 nm, ε=1.9×10^3 L mol^{-1} cm^{-1}) [20].

4. Analytical applications

The proposed method within the already established optimal conditions was used to determine the nickel content in tap water. The results presented in Table 3 indicate the successful applicability of the proposed method to the actual analysis of the sample.

Table 3: Determination results of nickel (II) in the sewage water ($n = 6$, $P = 0.95$)

Analysis object	Added, mg/L	Found, mg/L	Found in the sample, mg/L $\overline{X} \pm \dfrac{t_P \cdot S}{\sqrt{n}}$	S_r
Sample 1	4.0	4.48	0.48±0.05	0.05
Sample 2	7.0	8.12	1.12±0.11	0.08

4. Conclusion
1. The obtained results show that the newly developed method, which used Ph. TAD reagent, can be effectively used for the quantitative extraction and evaluation of Ni (II) from aqueous media.
2. Extraction of mixed ligand complexes is maximal at pH 4.2-6.0. The proposed method is fast and requires less organic solvent.
3. Optimal conditions for the formation and extraction of compounds were found and the ratio of the components in the complexes was determined.
4. The Beer Law was applied in the range of 0.5-15 µg / ml.
5. Simple, fast and sensitive methods proposed for determining trace amounts of Ni (II). The method is very accurate, faster and easier than other methods.

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