

Spectrophotometric Determination Of Nickel(II) Using 5-(2-Bromo-5-Methoxybenzylidene)-Thiazolidine-2,4-Dione

Kuliev K. A., Verdizade N. A., Alieva K.R.

Department of Chemistry, Azerbaijan State Pedagogical University

Correspondence to Author: K. A. Kuliev

Lecturer , Department of Analytical Chemistry, Azerbaijan State Pedagogical University

U. Gadjibekov street 68. Baku, AZ 1000, Azerbaijan

E-mail: kerim.kuliev.69@mail.ru

Abstract:

A simple and selective spectrophotometric method was developed for the determination of nickel(II) using 5-(2-bromo-5-methoxybenzylidene)-thiazolidine-2,4-dione (BMBT) as a chromogenic reagent forming a yellow brown complex at pH 8.5. The possibility of using BMBT for photometric determination of nickel(II) has been studied. The nickel(II) complex is formed in the pH range 7.1-8.9. The maximum analytical signal for the complexation of nickel with BMBT is observed at 482 nm. The molar absorption coefficient is 1.75×10^4 . The ratio of components in the complex is Ni: BMBT = 1:2. Obedience to the basic law of light absorption is observed at a cobalt concentration of 0.3-13 $\mu\text{g} / \text{ml}$. Based on the results of spectrophotometric studies of nickel(II) with BMBT, methods for determining nickel in different objects have been developed.

Key words: Spectrophotometry; nickel(II), 5-(2-bromo-5-methoxybenzylidene)-thiazolidine-2,4-dione

1. INTRODUCTION

Nickel is an essential nutrient for the human body, as well as for animals. In plant and animal organisms, nickel takes part in enzymatic reactions; it is able to accumulate in the feathers of birds. It is believed that this element has an impact on a person's well-being and health. With an excess of nickel in the body, tachycardia and anemia, pulmonary and brain edema, and allergic reactions may occur. Nickel is widely used in electroplating, the manufacture of Ni-Cd batteries, rods for arc welding, pigments of paints, ceramic, surgical and dental prostheses, magnetic tapes and computer components and nickel catalysts [1].

Nickel-containing sewage is harmful after ingress into water. This fact explained the importance of the monitoring of nickel concentration in natural and waste water samples. Flame and graphite furnace atomic absorption spectrometry and spectrophotometric methods provides accurate and rapid determination of nickel in natural and waste waters [2]. However, very frequently a direct determination cannot be applied due to low concentration of analyte or matrix interferences.

Several analytical methods have been used for nickel determination, including flame atomic absorption spectrophotometry [3], graphite furnace atomic absorption spectrometry [4], electrothermal atomic absorption spectrometry [5], atomic fluorescence spectrometry [6], inductively coupled plasma-optical emission spectrometry [7], and spectrophotometry [8,9,10,11,12]. However the above mentioned techniques involve relatively high operational costs of instruments or materials and high purity solvents.

The methods involving spectrophotometry are rather popular due to their simplicity, inexpensive instrumentation and easy automation. Nickel(II) chelates of several ligands like diphenylcarbazone, diphenylthiocarbazone, 8-quinolinol and its substituted analogues produce intense absorption in the optical spectra, in the visible range, which is characteristic of the ligand itself [13, 14, 15].

Mixed - ligand complexes with oxythiophenols and dithiophenols in the presence of hydrophobic amines used to develop methods for the determination of nickel in various objects [16-19]. We have studied the possibility of using 5-(2-Bromo-5-methoxybenzylidene)-thiazolidine-2,4-dione (BMBT) for the photometric determination of nickel(II).

2. Experimental

2.1. Reagents and Apparatus

The standard solution (1mg / ml) Ni(II) was prepared by dissolving in water an exact linkage $(\text{NH}_4)_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ in water containing 2 ml conc. H_2SO_4 and diluted with water to [15]. Reagents and Solutions

The working solutions were prepared just before use by dilution of the standard solution with redistilled deionised water. BMBT were synthesized according to the procedure [20]. The reagent solution (0.002 M) was prepared by dissolving accurately weight of pure reagent in sodium hydroxide (1 M). Freshly prepared solutions were used for all experiments. To create the optimal pH, 1M solutions of KOH and NaOH or Britton-Robinson buffer were applied (pH 5-12).

Structure of ligand was confirmed by using NMR and IR spectra [21, 22]. IR (KBr, cm^{-1}): 3364 (N-H); 2925 (Ar-H), 1674 (C=O), 1573 (C=N), 1449 (C=C), 1380 (C-N) 733 (C-S-C), $^1\text{H-NMR}$ (sDMSO-d_6) δ : 2.2 (6H, s), 7.18 (2H, s), 7.61 (1H, s), 9.16 (1H, s), 12.45 (1H, s).

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. 1% solutions of diverse ions were prepared by dissolving measured amounts of salts of the corresponding ions in distilled water. In some cases, acids were added to prevent hydrolysis.

2.2. Instrumentation

The absorbance of the extracts was measured using a Shimadzu UV1240 spectrophotometer (Japan) and KFK-2 photocolormeter (USSR). Glass cells with optical path of 10 or 5 mm were used. pH of aqueous phase was measured using an I-120.2 potentiometer with a glass electrode. Muffle furnace was used for dissolution of the samples. IR spectra were recorded on a spectrophotometer "Specord M80" (Germany). $^1\text{H-NMR}$ spectra were recorded on "Bruker" Fourier Transform (300,18 MHz) in C_6D_6 .

2.3. General Procedure

2.3.1. General procedure for the determination of nickel(II)

In a 10 mL volumetric flask, 1 mL of the solution containing 5-100 $\mu\text{g Ni}^{2+}$ and 2 mL of a 0.01 M 5-(2-bromo-5-methoxybenzylidene)-thiazolidine-2,4-dione reagent was added and the volume was adjusted to 10 mL with methanol. Absorbance was measured at 540 nm against the reagent blank ($l=0.5\text{cm}$). Calibration graphs were constructed by plotting the absorbance vs. Ni^{2+} concentration.

2.3.2. Determination of nickel(II) in steel

A weighed sample of 0.2 g was dissolved in 20 ml of H₂SO₄ (1:1) was oxidized with a few drops of concentrated HNO₃ and evaporated twice to vapor SO₃. The precipitated salt was dissolved in 20 ml of 15% tartaric acid under heating, the solution was cooled, adjusted with water to 100 ml in a volumetric flask, stirred and filtered. An aliquot of 5 ml was put into a separatory funnel and was determined nickel using the proposed procedures.

2.3.4. Determination of Ni(II) in sewage water and bottom sediments

1l taken for analysis of waste water is evaporated to obtain a precipitate, do not boil. The precipitate was dissolved in 5 ml of concentrated HNO₃, was transferred to a 50 ml flask and diluted to the mark with water.

3. Results and Discussion

3.1. Selection of the reaction solvent

BMBT forms a stable red yellow-brown complex with Ni(II) in some aqueous and non-aqueous solvents. A suitable solvent can be a solvent that can dissolve both the BMBT reagent and the Ni-BMBT complex. In addition, acceptable absorption spectra for the complexes formed should be observed without reagent interference. This study used water (base medium), methyl alcohol, ethyl alcohol, chloroform, hexane, dichloromethane, and acetonitrile. The best results were obtained using methanol as a suitable solvent.

3.2. Effect of pH

The complex is formed in the range of pH 2.6-10 (pH_{opt}=7.1-8.9). With a decrease in the pH of the aqueous phase, the extraction of Ni(II) gradually decreases, which is obviously associated with a decrease in the concentration of the ionized form BMBT and, most likely, in solution it is in undissociated form. At pH 10.5, the complex is practically not formed, which is apparently due to the hydrolysis of the nickel ion. The optimal condition for the formation and extraction of the complex is 5×10⁻⁴ mol / l concentration of BMBT.

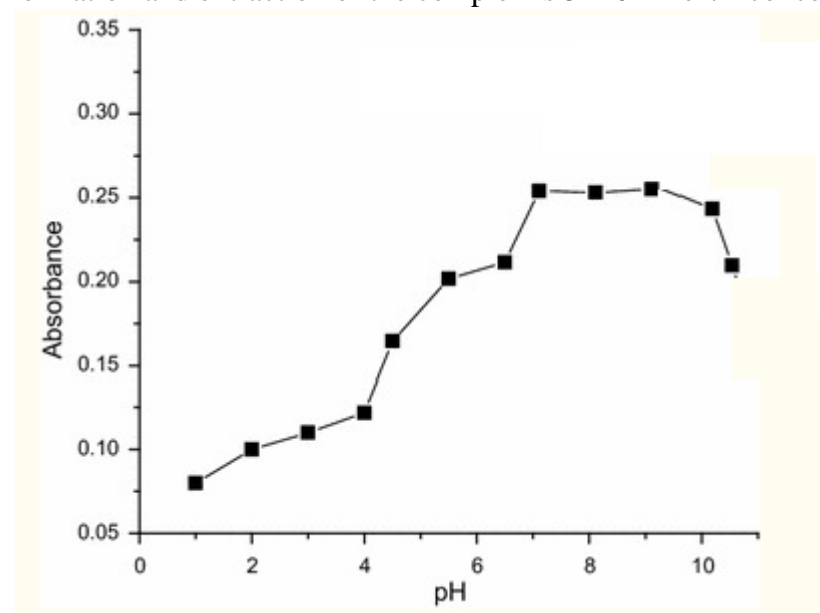


Fig.1. The dependence of the optical density of the complex on the pH of the aqueous phase. C_{Ni(II)}=3.44×10⁻⁵ M; C_{BMBT} = 5.0×10⁻⁴ M; KFK-2, λ=490 nm l = 1 cm

The complex of nickel with BMBT is stable in aqueous and organic solvent and does not decompose for two days. Maximum light absorption is achieved within 5 minutes. The complex is stable when heated to 80° C.

3.3. Absorption spectra of reagent solutions and metal complexes

The absorbance of the reagent solution was measured against water blank. The maximum analytical signal in the complexation of nickel with BMBT is observed at 482 nm. BMBT maximally absorbs at 336 nm. Bathochromic shift is 146 nm. The molar absorption coefficient is 1.75×10^4 .

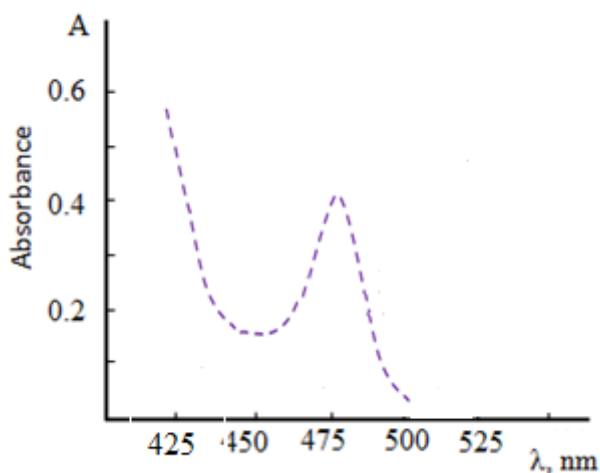


Fig.2. Absorption spectra

$C_{Ni(II)}=3.44 \times 10^{-5} M$; $C_{BMBT} = 5.0 \times 10^{-4} M$; $C_{\Phi-26}$, $l = 1 \text{ cm}$

3.4. Stoichiometry of Ni(II) - BMBT complexes

The chemical structure of Ni(II) - BMBT complex was determined equilibrium shift, the relative output of Starik Barbanel and the straight line methods [23]. All methods showed that the ratio of components in the complex is Ni: BMBT = 1:2. The data of these were utilized to calculate stability constant of complex.

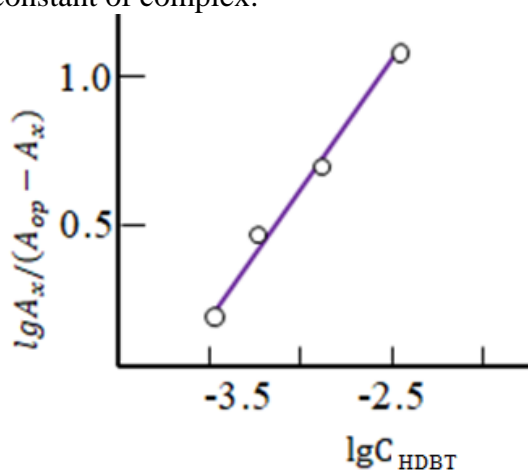


Fig. 3. Determination of the ratio of components by equilibrium shift method

$C_{Ni(II)}=3.44 \times 10^{-5} M$; $C_{\Phi-26}$, $l=1 \text{ cm}$.

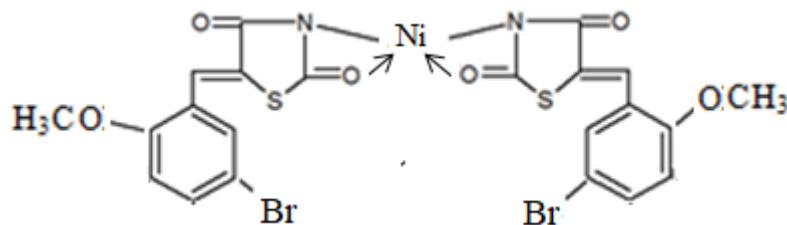
The Ni(II) complex with BMBT was synthesized and investigated by chemical analysis and IR spectroscopy. The IR spectrum of the complex is compared with the spectrum of the reagent. The observed band in the region of 1593-1448 cm^{-1} corresponds to the aromatic ring (C = C). In the IR spectra of the complex in the region of 3050-3020 cm^{-1} there are strong absorption bands associated with ν_{CH} in the aromatic core. The IR spectra of the BMBT shows $\nu(\text{C}=\text{S})$ band at 1320 cm^{-1} , $\nu(\text{C}=\text{N})$ band at 1590 cm^{-1} .

The absorption bands at 830–720 cm^{-1} can be attributed to C-H deformation vibrations, the absorption bands at 1630–1460 cm^{-1} to the stretching vibrations of phenyl rings, and the absorption bands at 1370 cm^{-1} to $\nu_{(\text{CN})}$. ν_{CS} is observed at 685 cm^{-1} , and ν_{CO} is observed at 1291 cm^{-1} . The absorption bands at 450 cm^{-1} and 575 cm^{-1} correspond to $\nu(\text{Ni}-\text{O})$ and $\nu(\text{Ni}-\text{N})$, respectively [21,22]. The disappearance of the absorption band in the region of 3500–3250 cm^{-1} with a maximum at 3364 cm^{-1} indicates the absence of free -NH groups in the synthesized complex. This indicates that metal is kovalently bonded with nitrogen and coordinate bonded with oxygen.

A thermogravimetric study of the Ni-BMBT complex showed that its thermal decomposition occurs in two stages. The dehydration temperature (90° - 115° C) on the DTA curve by the endothermic effect (weight loss 4.93%) indicates the dehydration of the complex. In the temperature range of 385-450°C, the maximum rate of mass loss is observed, which is associated with the removal of BMBT (weight loss 41.78%). The end product of thermolysis of the complex is NiO.

It was established that Ni^{2+} is the complexing form of nickel [24, 25]. In this case, the number of hydrogen atoms displaced from one BMBT molecule turned out to be equal to 1.

Based on the ratio of components in the resulting complexes, the number of protons being displaced, and the ionic form of nickel, one can imagine the probable structure of the complexes on Ni-BMBT



It was established that with BMBT the colored complexes also form ions of Fe(III), Cu(II), Mo(VI), Se(IV), Pt(II), Mn(II), Cd(II), Zn(II), Pb(II) and Pd(II). The selectivity of the determination increases significantly in the presence of masking agents or when the pH of the medium changes. Large amounts of fluoride, chloride, bromide, oxalate, thiosulfate, sulfate, acetate, tartrate, and citrate ions do not interfere with the determination. Thiocyanate, thiourea and phosphate ion interfere, even when present in small quantities, whereas EDTA masks nickel (II) completely due to the higher stability of the Ni(II)-EDTA complex. The interference of Zn(II), Pb(II) Se(IV), Ce(IV), Cu(II), Cd(II) and Pd(II) can be eliminated by using 1.0 ml of 0.5% thiosulphate solution.

3.5. Beer's law and sensitivity of Ni(II) – BMBT

A calibration graph for the determination of copper was prepared under the optimum experimental conditions. The Ni(II)-BMBT system obeys Beer's law in the concentration range of 0.3–13 $\mu\text{g/mL}$ with the equation $A_{482} = 0.045 + 0.071x$. The data obtained for the construction of the calibration curve were processed by the method of least squares [26].

3.6. Analytical applications

Based on the equation of the calibration graphs, the limit of photometric detection and the limit of quantitative determination of cobalt were calculated. In tab. 1 shows the main spectrophotometric characteristics of the method for determining Ni(II) with BMBT.

Table 1. Formation conditions and some chemical and analytical properties of Ni(II) with BMBT

Parameter	Value
Color	yellow brown
pH _{Op}	7.1-8.9
λ_{\max} (nm)	482
Bathochromic shift	146
Molar absorptivity ($L \cdot mol^{-1} \cdot cm^{-1}$)	$1.65 \cdot 10^4$
Sandell's sensitivity ($ng \cdot cm^{-2}$)	3.51
The equation of calibration curves	$0.045+0.071x$
Correlation coefficient	0.9954
Stability constant (β)	10.61
Beer's law range ($\mu g \cdot ml^{-1}$)	0.3-13
Limit of detection (LOD): $ng \cdot mL^{-1}$	12
Limit of quantification (LOQ): $ng \cdot mL^{-1}$	39

In tab. 2 shows the data allowing to compare the analytical characteristics of the photometric nickel(II) methods developed by us with some already known [3, 9, 18] methods. As can be seen from the table, the methods proposed by us are quite selective, sensitive, they are expressive and allow to determine even small amounts of these metals and to obtain reproducible results. The proposed method compares favourably with the existing ones (Table 3) and offers the advantages of better simplicity, rapidity, sensitivity and selectivity.

Table 2. Comparative characteristics of the procedures for determining nickel

Reagent	pH	λ , nm	$\epsilon \cdot 10^{-4}$	Beer's law range ($\mu g \cdot ml^{-1}$)
Dimethylglyoxime [28]	12	470		0.26-2.1
N-ethyl-3-carbazolecarboxaldehyde-3-thiosemicarbazone.[29]	6.0	400	1.114	
7-Methyl-2-chloroquinoline-3-carbaldehyde thiosemicarbazone [30]	6.0	410	1.67	
Thiazole-2-carbaldehyde 2-quinolyldiazine [31]	8.7-9.5	522	7.17	0-0.7
Pyridoxal-4-phenyl-3-thiosemicarbazone [32]	4-6	430	1.92	0.5-5
4-gidroksibenzal'degid-4-bromfenilgidrazin [33]	4.0	497	12.85	0.01-0.1
BMBT	7.1-8.9	482	1.75	0.3-13

Based on the results of spectrophotometric studies of nickel(II) with BMBT, methods for the determination of nickel in plants have been developed. In sewage and bottom sediments (tab. 3 and 4) The proposed method under the already established optimum conditions was applied for the determination of Ni(II) in various objects. The results presented in Table 4 and Table 5 indicate the successful applicability of the proposed method to real sample analysis.

Table 3. Determination of nickel in steel 8XΦ (C16⁶) (n=5, P=0.95)

Reagent.	\bar{X} , %		S _r	μ
Dimethylglyoxime	0.255	0.0065	0.024	0.2550±0.0065
Ni - BMBT	0.257	0.0114	0.042	0.2570±0.0114

Table 4. Determination results of nickel(II) in the sewage water and bottom sediments (n = 6, P = 0.95)

Analysis object	Added,	Found,	S _r	Found in the sample, μ / kg
Sewage water				
Sample 1	2.0	2.55	0.08	0.550±0.045
Sample 2	5.0	6.64	0.06	1.640±0.097
Bottom sediments				
Sample 1	2.0	3.46	0.07	1.460±0.105
Sample 2	5.0	5.25	0.05	2.250±0.060

4. Conclusions

The results obtained show that the newly developed method in which the reagent 5-(2-bromo-5-methoxybenzylidene)-thiazolidine-2,4-dione (BMBT) was used, can be effectively used for quantitative determination of Ni(II) in aqueous media. Complex of nickel(II) with BMBT have been investigated by spectrophotometric method.

Complex is maximal formed at pH 7.1-8.9. The proposed method is quick and requires less volume of organic solvent. The optimal conditions for the complex formation and the ratios of components in the complexes have been determined. The Beer's law was applicable in the range of 0.3-13 μg/ml. A simple, rapid and sensitive methods proposed for the determination of trace amounts of nickel. The developed techniques are used to determine nickel in bottom sediments and in steel.

References

- Merian E., Anke M., Stoppler M., Wiley-VCH: Weinheim; Vol.2, (2004). Elements and Their Compounds in the Environment
- Ravichandran C., Benzil D., Ramachandraiah C. Chandrasekhar K. B. Extraction and spectrophotometric determination of nickel in water, alloys and edible oil samples International Journal of Bioassays 4.11 (2015): 4468-4472
- Avcı H., Kaya G., Akdeniz I., Ince M., Yaman, M. Flame atomic absorption spectrometric determination of nickel and chromium in various plant leaves used as biomonitors in environmental pollution. Fresenius Environmental Bulletin, (2013) 22(2), pp. 379-387.
- Dobrowolski R., Otto M. Determination of nickel and cobalt in reference plant materials by carbon slurry sampling GFAAS technique after their simultaneous preconcentration onto modified activated carbon. Journal of Food Composition and Analysis, 2012, 26(1-2), pp. 58-65
- Sadeghi O., Tavassoli N., Amini M. M., Ebrahimzadeh H., Daei N. Pyridine-functionalized mesoporous silica as an adsorbent material for the determination of nickel and lead in vegetables grown in close proximity by electrothermal atomic adsorption spectroscopy. Food Chemistry, 2011, 127 (1), pp. 364-368
- Zeng, C., Jia, Y., Lee, Y.I., Hou, X., and Wu, L. Ultrasensitive determination of cobalt and nickel by atomic fluorescence spectrometry using APDC enhanced chemical vapor generation. Microchemical Journal. 2012, 104, pp. 33-37

7. Beiraghi A., Babae S., Roshdi M. Simultaneous preconcentration of cadmium, cobalt and nickel in water samples by cationic micellar precipitation and their determination by inductively coupled plasma-optical emission spectrometry. *Microchemical Journal*, 2012, 100, pp. 66-71
8. Ravichandran, C. Extraction and spectrophotometric determination of nickel in water, alloys and edible oil samples / C.Ravichandran, D. Benzil, C.Ramachandraiah [et al.] // *International Journal of Bioassays*, -2015. V.4, №11, -p.4468-4472.
9. Ramachandraiah, C. Development of a highly sensitive extractive spectrophotometric method for the determination of nickel(II) from environmental matrices using N-ethyl-3-carbazolecarboxaldehyde-3-thiosemicarbazone / C.Ramachandraiah, J.R. Kumar, K.J. Reddy [et al.] // *Journal of Environmental Management*, -2008. V.88, №4. -p.729-736.
10. Amin, A.S., AL-Attas, A.S. Study of the solid phase extraction and spectro-photometric determination of nickel using 5-(4-chlorophenylazo)-6-hydroxypyrimidine-2,4-dione in environmental samples // *Journal of Saudi Chemical Society*, -2012. V. 16, №4, -p.451–459.
11. Chimpalee, N., Chimpalee, D., Keawpasert, P., and Thorburn Burns, D. Flow injection extraction spectrophotometric determination of nickel using bis(acetylacetonate)ethylenediimine. *Analytica Chimica Acta*, 2000, 408 (1-2), pp. 123-127.
12. Malik A. K., Rao, A.L.J. Spectrophotometric determination of cobalt, nickel, palladium, copper, ruthenium and molybdenum after extraction of their isoamyl xanthate complexes into molten naphthalene. *Journal of Analytical Chemistry*, 2000, 55 (8), pp. 746-749.
13. Suresh T., Kumar S. S., Kottureshawara N. M. et al. Spectrophotometric study of nitrogen base adducts of nickel(II)-4-methyl-8-quinoline. *E-Journal of Chemistry* 2008, V. 5, No.2, pp. 404-408.
14. Umland, F., Janssen A., Thierig D., Wünsch G. Theorie und praktische anwendung von complexbildnern. Frankfurt am Main, Akademische Verlagsgesellschaft. 1971.
15. Marczenko, Z., and Balcerzak, M. Metod'y spektrofotometrii v UF I vidimoy oblastiakh v neorganicheskom analize. Moskov, Binom. Laboratoriya znanij. 2007.
16. Zalov Ali Z. Gavazov Kiril B. Extractive Spectrophotometric determination of nickel with 2-hydroxy-5-iodothiophenol and diphenylguanidine. *Chemistry Journal* (2014), V. 04, Issue 5, 20-25
17. Kuliev K.A., Verdizade N. A., Aliev S. G., Suleymanova G. S. and Mamedova Sh. A. Efendieva N. N Complex formation in a liquid-liquid extraction system containing nickel (II), 2,6-dithiol-4-ethylphenol and bathophenanthroline. *World Journal of Pharmaceutical Research*. V. 7, Issue 19, 2018. DOI : [10.20959/wjpr201819-13762](https://doi.org/10.20959/wjpr201819-13762) 61-73
18. Zalov A.Z., Shiraliev S. M., Askerova Z. Q. Extraction-spectrophotometric study on the complex formation in the nickel(II) - 4-hydroxy-3-thiolbenzoic acid - diphenylguanidine system *Indo American Journal Of Pharmaceutical Sciences*. 2018, 05 (12), 15681-15689
19. Kuliev K.A., Mamedova R. A. Ismailova Sh. Y. Complex formation in a liquid-liquid extraction system containing nickel(II), 2,6-dithiol-4-methylphenol, and diphenylguanidine/ *Journal of Multidisciplinary Engineering Science and Technology (JMEST)*. 2016, V. 3, № 9 5510-5521
20. Pinheiro DS, Junior ENS, Consolini G, et al. Optimized synthesis and characterization of thiazolidine-2,4-dione for pharmaceutical application. *MOJ Biorg Org Chem*. 2017;1(4):122–126. DOI: 10.15406/mojboc.2017.01.00022
21. Nakamoto, K. *IK-spectr KR neorganicheskikh i koordinatsionnykh soedinenii (Infrared and Raman Spectra of Inorganic and Coordination Compounds)*. Moscow : Mir, 1991. P 536.

22. Bellami, L. Infrakrasnie spectri slojnikh molecule (The infra-red spectra of complex molecules). Moscow: Mir, 1991. P. 592.
23. Bulatov M. I., Kalinkin I. P., *Practicheskoe rukovodstvo po photocolorimetriceskim i spectrophotometriceskim metodam analiza*, Leningrad, 1976.
24. Akhmedly, M. K., Kly'gin, A. E., Ivanova, L. I., Bashirov, E. A. On the chemistry of interaction of gallium ions with a number of sulphophtaleins. *Zhurnal Neorganicheskoi Khimii*, 1974. V.19.№8. pp. 2007-2012.
25. Nazarenko V. A. Tr. Komis. po analit. khimii Akad. Nauk SSSR (Proc. Commission on Analytical Chemistry of the USSR's Academy of Sciences), 1969, Moscow: Nauka, vol. 17. p. 22.
26. Nazarenko, V. A., Biryuk, E. A.. A study of the chemistry of reactions of multivalent element ions with organic reagents. *Zh. Anal. Khim.*, 1967. V.22 № 13, pp.57-64.
27. Dorokhova Ye. N., Prokhorova G. V. *Analiticheskaya khimiya (fiziko-khimicheskiye metody analiza)*. M.: Vysshaya shkola, 1991. s. 250.
28. Yoshikuni N., Baba T., Tsunoda N., Oguma K.. Aqueous two-phase extraction of nickel dimethylglyoximate complex and its application to spectrophotometric determination of nickel in stainless steel. *Talanta*. 2005, V. 66, No 1, P. 40–44
29. Ramachandraiah C, Kumar J. R, Reddy K. J, et.al.. Development of a highly sensitive extractive spectrophotometric method for the determination of nickel(II) from environmental matrices using N-ethyl-3-carbazolecarboxaldehyde-3-thiosemicarbazone. *J Environ Manage* 2008 V;88:№4, pp.729-736.
30. Jadhav V.A., Kulkarni M.U. 7-Methyl-2-chloroquinoline- 3-carbaldehyde thiosemicarbazone as analytical reagent for copper, cobalt and nickel (II). *J Indian Chem Soc* 1992; 69: 287–8.
31. Makoto O., Tsuyoshi W., Mitsuru M. Solvent Extraction and Spectrophotometric Determination of Nickel(II) with Thiazole-2-carbaldehyde 2-Quinoline-lylhydrazone *Analytical Sciences*. Vol. 2 (1986) No 6, pp. 549-552
32. Sarma L. S., Kumar J. R., Reddy K. J. et al. Development of highly sensitive extractive spectrophotometric determination of nickel(II) in medicinal leaves, soil, industrial effluents and standard alloy samples using pyridoxal-4-phenyl-3-thiosemicarbazone. *Journal of Trace Elements in Medicine and Biology*, 2008, 22, pp. 285–295
33. Rekha D., Kumar J. D., Jayaraj B. et al. Nickel(II) determination by spectrophotometry coupled with preconcentration technique in water and alloy samples. *Bull. Korean Chem. Soc.* 2007, V. 28, No. 3 pp. 373-378