Application Of Oxyazo Compounds In The Definition Of The Ion Bi (V)

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Abstract: The paper presents the experimentally obtained optimal conditions for the reaction of immobilization and complexation of Bi (V) with reagents TN-15 (2-oxo-5,6-dimethylthieno [2,3] -pyrimidin-4-one) and TN-249 (2-N-5-methyl-6-ethoxycarbonylthieno [2.3-d] pyrimidin-4-one). The dependence of the analytical signal on the nature, concentration and pH of the medium of the reacting components was established, the composition of the complex (Me: R), the molar coefficient of light absorption of the complex (MeR2) and the reagent (HR) were determined, the dissociation constant of the reagent and other physicochemical characteristics were determined. The possibility of the sorption-spectroscopic determination of Bi (V) was shown and the conditions for the selective sorption-spectroscopic determination of Bi (V) in the presence of foreign ions were optimized.

Keywords:sorption spectroscopic determination, 2-oxo -5,6-dimethylthieno [2,3] -pyrimidin-4-one, 2-N-5-methyl-6-ethoxycarbonylthieno [2.3-d] pyrimidin-4-one , immobilization.

1. RELEVANCE OF THE TOPIC

The current state of the development of science, technology and industry requires the development of sensitive, selective and labor-intensive methods for the determination of bismuth, since the fields of application of bismuth are constantly expanding. Currently, the scale of human economic activity has led to a serious exacerbation of the ecological situation. An important role in solving these problems is the selection of spectroscopic methods for the determination of microconcentrations of bismuth ions using organic reagents related to oxyazo compounds.

Today, in analytical chemistry, the role of test methods as selective, express and not requiring complex hardware design methods for the detection of elements, as well as their semi-quantitative and sometimes quantitative determination, is increasing. The main analytical signal when evaluating test samples is color, the change of which occurs due to chemical reactions involving the analyte. The nature of the color change is observed visually (using a known set of comparison samples), however, in order to document the determination results and to minimize the method errors, it is necessary to present the quantitative characteristics of

the color of the analyzed samples. The use of computer technology makes it possible to develop color estimation algorithms to solve specific research and production problems.

2. EXPERIMENTAL PART

Apparatus and utensils used: Electronic analytical balance type ED 124S max 120g d = 0.1 (0.0001) g No. 21810978; analytical scales XA-21; scales technical BM-200; concentration photocolorimeter LFL-2; spectrophotometer UV-1800 (UV-Spectrotometr, Shimadzau); magnetic stirrer (RSM-0.1 HS, Phoinx instrument); universal ion meter EV-74; pH meter PB-1121754333 No. 10207801 1-14 pH; ultrasonic mixer (Bandelin Sonerx Digitec); drying oven (ZXRD-B5055, LABWIT).

Cuvettes with an absorbing layer thickness of 0.5-3.0; volumetric flasks GOST 1770. second class of accuracy, with a capacity of 5 cm^3 – 1000cm^3 ;graduated pipettes, GOST 20292, second class of accuracy, with a capacity of 0.1 cm^3 - 25 cm^3 ;cchemical takans, with a capacity of 5 cm^3 -100 cm^3 ; measuring cylinders 10 ml - 100 ml; polyethylene and glass dishes for storing reagents; burettes 25cm^3 , 50 cm^3 ;conical flasks with a volume of 100 cm^3 - 500 cm^3 .

Reagents and substances used: TN-15 (2-oxo-5,6-dimethylthieno [2,3] pyrimidin-4-one); TN-249 (2-H-5-methyl-6-ethoxycarbonylthieno [2.3-d] pyrimidin-4-one); distilled water, GOST6709; nitric acid (chemically pure), GOST 4461-67; hydrochloric acid (chemically pure), GOST 3118-77; acetic acid (chemically pure), GOST61-69; hydrochloric acid (chemically pure), GOST 3118-77; sodium hydroxide (reagent grade), GOST 4228-66; copper sulfate (chemically pure), GOST 4165-78; cadmium chloride (chemically pure), GOST 4437-6121; ferric chloride (chemically pure), GOST 4147-48; nickel chloride (chemically pure), GOST 4123-58; zinc chloride (chemically pure), GOST 4768-32; bismuth salts. Polymersorbentsbasedonnitronfiber.

Preparation of the solutions used: for the experiments, standard Bi (V) solutions were prepared with a concentration of 1.0 mg / cm ^{3}, which were prepared by dissolving from the corresponding mass of metal (99.99%) when heated in a mixture of 10 cm^{3}concentrated nitric and hydrochloric acids "chemically pure" according to a well-known technique. Then the resulting mixture was heated to boiling to remove nitrogen oxides, after which it was cooled, the resulting solutions were transferred into volumetric flasks at 50.0 and 100.0 cm^3 and the volume was brought up to the mark with distilled water.

Standard solutions of iron (II and III), lead, copper, zinc, chromium, cobalt, aluminum, zinc, nickel and manganese with a concentration of 1.0 g / dm^3 was prepared by dissolving the corresponding metals in mineral acids or their salts in bidistilled water. Solutions of lower concentrations of the studied metals were prepared by successive dilution of their strong solutions with bidistillate before starting work. To prepare standard solutions of some other heavy and transition metals, we took exact weighed portions of their nitric acid salts (reagent grade) and dissolved them in bidistillate. Buffer solutions were prepared according to the

method described in the reference books, 25 ml flasks were taken, a Bi (V) solution (40 μg / ml) was poured, then 1.0 ml of 0.0005 M TN-15 reagent was added to it and 10 ml of buffer solution was added. Solutions of buffers and with reagent TN-249 were prepared in a similar way.

3. RESULTS AND ITS DISCUSSION

The immobilization of complexes on the studied sorbents was carried out from aqueous solutions in a static mode according to the following procedure: a fiber sample in the form of disks (tablets) 2 cm in diameter and weighing 20-60 mg was pressed under a pressure of 150-300 kg / cm^3 in a special form and immersed in a glass with 0.1 M HCl solution (50 cm^3). In this case, the original sorbent transforms into the chloride form. After that, the carrier was washed with distilled water, and then dipped into a glass with 10 cm^3 a solution containing an organic reagent and a metal ion selected for immobilization and kept it for the required period of time. Holding the carrier with a glass rod, the remaining complex was decanted, and the fiber was washed with distilled water (2 times 50 cm^3) to remove the unattached complex and keep the media in Petri dishes in a wet state. The amount of the immobilized complex was determined by its residual concentration in the flushing waters by the photometric method or by the method of reflection spectroscopy by taking the diffuse reflection spectra of the disk.

Determination of the charge of the complexa) 1.0 g of the KU-2 cation exchanger was transferred into a column with a diameter of 1.0 cm and treated 3 times with 10.0 ml of 0.1 N hydrochloric acid solution and washed with 50.0 ml of distilled water until neutral. Then, under optimal conditions, 1.0 ml of a 0.1% solution of reagents, 1.0 ml (50 μg / ml) of a Bi (V) solution, 10.0 ml of a buffer solution were poured into a 25.0 ml volumetric flask and brought to distilled water marks. 10.0 ml of the complex solution was passed through the KU-2 cation exchanger.

b) 1.0 g of the AN-17 anion exchanger was transferred into a column with a diameter of 1.0 cm, and treated 3 times with 10.0 ml of 0.1 N NaOH solution and washed out the column with 50 ml of distilled water until neutral, then 10 ml of the solution was passed through complex.

Sorbent preparation for work: the fibrous material is a fairly convenient, mechanically stable sorbent as a solid phase. It is a weakly dyed polyacrylonitrile fiber modified with hexamethyl, stable in the range of media to alkaline, having good kinetic and ion-exchange characteristics, and easy to use. Fibrous sorbent is used both in static and dynamic modes, it is easily carried with tweezers, does not deform when stirring, heating in a solution and other operations. This sorbent was selected from various types of sorbents because it has strong basic properties.

To study the interaction conditions for the determination of the quantitative characteristics of the determination of Bi (V), it was necessary to select the optimal cuvette. For this, the optical density of TN-15 and TN-249 was measured on an SF device with different cuvette thicknesses. A solution of distilled water was used as a reference solution. The results are shown in Table 1.

Table 1.

Selection of the optimal cuvette for TN-249 and TN-15 reagents

Reagent	Cuvette cm ^{3}	λmax,nm	315	364	400	440	490	540	590
TN-15	0,3		0,23	0,195	0,145	0,15	0,059	-	-
	0,5	A	0,21	0,26	0,2	0,225	0,27	0,12	-
TN-249	0,3		0,17	0,33	0,42	0,45	0,31	0,054	0,046
	0,5	A	0,35	0,5	0,65	0,7	0,47	0,1	-

When measuring the optical density of the reagents TN-15 and TN-249 at different cuvette thicknesses, it was found that the maximum optical density is observed when the cuvette thickness is 0.5 cm.

To select the optimal wavelength, the optical density of the TN-15 solution was measured andBi(V)and also a solution of TN-249 and Bi (V) at different wavelengths. The data obtained are shown in table. 2 and fig. 1.

Table 2. Finding the optimal wavelength of the Bi (V) complex (l = 0.5cm)

Reagent	λmax, nm	315	364	400	440	490	540	590
TN-15		0,58	0,38	0,25	0,26	0,24	0,14	0,10
TN-249	A	0,22	0,25	0,15	0,13	0,232	0,5	0,006
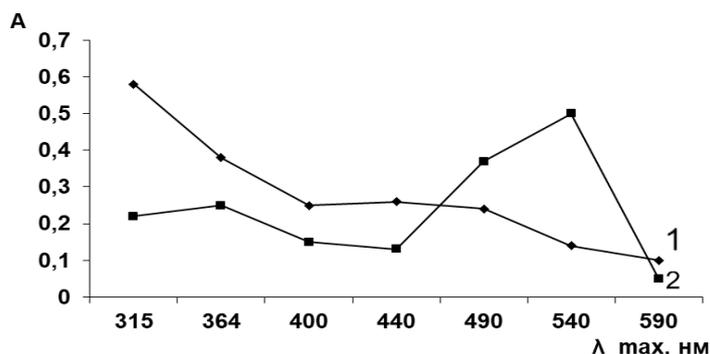
Figure: 1. Finding the optimal wavelength of the complex
1)TN-15 и Ag
2) TN-249 и Ag

From table. 2 and fig. 1 that the maximum optical density is achieved for the TN-249 complex with Bi (V) at a wavelength of 540 nm and TN-15 with Bi (V) at a wavelength of 315 nm.

To determine the optimal pH, a universal buffer solution was prepared with different pH values.

Method for preparing a solution for analysis: Into 50 ml volumetric flasks. poured in 1.00 ml of Bi (V) solution, 1 ml. 0.0005 M TN-249 solution and 10 ml. buffer solution with different pH values and brought the volume to the mark with distilled water. The same was done for the TN-15 reagent. Optical density was measured at SF. The data obtained are shown in table. 3.

Table3. 3dependence of the optical density of a bismuth complex solution reagents TN-249 and TN-15 from the pH of the solution

pH	2	3	4	5	6	7	8	9
TN-249 λ=540	0,212	0,25	0,23	0,33	0,32	0,32	0,298	0,27
TN-15 λ=315	0,13	0,19	0,165	0,10	0,11	0,12	0,11	0,10

The table shows that the optical density of the complex increases with increasing pH of solutions. The maximum optical density for the TN-249 and Bi (V) complex is observed at pH = 5, and for the TN-15 and Bi (V) complex at pH = 3. Based on this, pH = 3 and pH = 5 were chosen as optimal.

To establish the dependence of the optical density of solutions of buffer mixtures, a number of solutions were prepared with the same pH = 3, for the TN-15 complex with Bi (V) and pH = 5 for the TN-249 and Bi (V) complex, but with different buffer solutions of phosphate, acetate , universal.

We took 25 ml flasks and poured 1 ml Bi (V) (40 μg / ml), 1 ml 0.0005 M TN-249 solution, 10 ml into each flask with various buffer solutions with pH = 5. The same was done in the case of the TN-15 reagent, with different buffer solutions at different pH and the volume was brought to the mark. The data obtained are shown in Tables 4 and 5.

Table 4.
Selection of a buffer solution for the TN-15 complex with Ag

Buffer	pH	A1	A2	A3	À
Phosphate	3,42	0,14	0,13	0,13	0,13
Universal	3,2	0,19	0,19	0,19	0,19
Acetate	3,24	0,14	0,14	0,12	0,13

It can be seen from the tabular data that the maximum yield of the complex is observed when using a universal buffer solution (pH = 3.2), which was used for further studies.

Table 5
Selection of a buffer solution for the TN-249 complex with Ag

Buffer	pH	A1	A2	A3	À
Phosphate	5,4	0,41	0,41	0,41	0,41
Universal	5,2	0,33	0,32	0,33	0,33
Acetate	5,42	0,24	0,24	0,25	0,24

The tabular data shows that the maximum yield of the complex is observed when using a phosphate buffer solution (pH = 5.4), which was used for further research.

We have found that the fiber remains stable after sorption of the complex for several days.

Analysis method: In 25 ml volumetric flasks, 1.00 ml of Bi (V) solution, 1 ml was added. 0.0005 M TN-15 solution and 10 ml. buffer solution with different pH values and brought the volume to the mark with distilled water. The same was done for reagent TN-249. Then, a certain volume of reagent was poured into 50 ml beakers and carriers with a mass of -20 mg were lowered there. After a certain period of time, the fibers were taken out and washed with distilled water. Optical density was measured on a UV-1800 spectrophotometer (UV-Spectrotometr, Shimadzau) (Table 6 and Fig. 2.).

Table 6.

Measurement of optical density after immobilization

λmax, nm	364	400	440	490	540	590
TN-15- Bi(V) CMA-1	0,056	0,1	0,11	0,057	0,055	-
TN-249 - Bi(V)-CMA-1	-	0,25	0,26	0,25	0,2	0,059
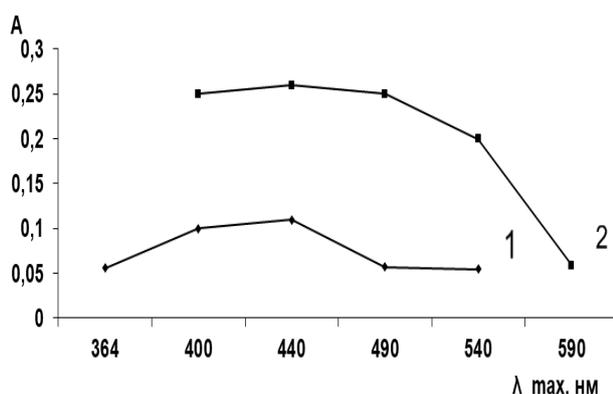
Fig. 2. Measurement of optical density after immobilization

1) TN-15

2)TN-15

From table 6 and fig. 2 that the measurement of optical density after immobilization showed that the maximum analytical signal on the carrier and in the solution coincide, which indicates the analogy of complexation in solution and on the fiber.

Dependence of immobilization on the contact time of the phases. Under statistical conditions, the contact time of the phases is an important factor ensuring the complete extraction of the substances of interest from the solution. To determine the color stability of the Bi (V) complex over time, the optical density of the solution was measured at certain time intervals.

4. METHODOLOGY:

1.0 ml (T = 50 μg / ml) of Bi (V) solution, 2 ml of 0.1% reagent solution, 10 ml of phosphate buffer solution for TN-15 were poured into volumetric flasks with a capacity of 25 ml and the volume was brought to the mark distilled water. The same was done with the universal buffer solution for the TN-249 reagent. The optical density of the complex solutions was measured relative to the blank solution on a UV-1800 spectrophotometer (Table 7).

Table 7.

Time dependence of immobilization for bismuth complex with TN-15 ($\lambda = 440$nm) and TN-249 ($\lambda = 315$nm)

t min.	5	10	15	20	25	30	40	60
TN-15	0,51	0,51	0,50	0,49	0,49	0,51	0,5	0,51
TN-249	0,22	0,22	0,21	0,2	0,22	0,22	0,22	0,22

From table 7 it can be seen that o.p. complex does not change over time, which makes it possible to obtain reproducible results.

To study the dependence of optical density on the amount of added reagent, a series of solutions was prepared in the following sequence, 1 ml of Bi (V) was poured into 25 ml volumetric flasks, and a variable amount of reagent TN-249 and TN-15 was added from 0.2 to 5 ml and 10 ml. universal buffer solution for reagent TN-15, 10 ml of phosphate buffer for reagent TN-249 and made up to the mark with water and measured the optical density on SF (Tables 8 and 9, Figures 3 and 4).

Table 8.

Dependence of the optical density of the TN-15c Bi (V) complex on the amount of added reagent ($\lambda = 315$ pH = 3.2 universal buffer)

Vreagent ml.	0,4	0,6	0,8	1,0	1,2	1,5	2,0	3,0
A	0,1	0,13	0,17	0,22	0,25	0,30	0,41	0,43
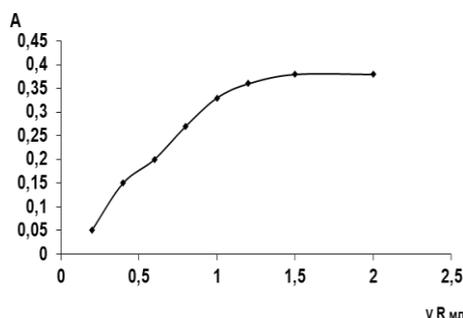
Fig. 3 Dependence of the optical density of the Bi (V) complex with TN-15 on the amount of added reagent..

Table 9

The order of merging components for TN-15 with Bi (V)

($\lambda = 540$ pH = 5.4 Phosphate Buffer VR = 2.0ml)

№	Drain procedure	A_1	A_2	A_3	
1	Bi-Phosphate buffer - **TN-15**	0,33	0,34	0,34	0,33
2	Ag- **TN-15** - Phosphate buffer	0,42	0,41	0,42	0,42
3	**TN-15** -Ag- Phosphate buffer	0,27	0,26	0,26	0,26

From the obtained experimental data (Table 10), it can be seen that the maximum optical density is observed in the second order of merging of the components, therefore, for the

convenience of the experiment, it was the second order of merging of the components (Bi-TN-15 - phosphate buffer) was chosen. In further studies, this order of merging of the components was used as the optimal one.

Table 11.

The order of merging components for TN-249 with Bi (V)

($\lambda = 315$, pH = 3.2 universal buffer, VR = 1.5 ml)

№	Drain procedure	A_1	A_2	A_3	À
1	Bi(V) -universal buffer - TN-249	0,44	0,45	0,45	0,45
2	Bi(V) - TN-249 -universal buffer	0,37	0,37	0,38	0,37
3	TN-249 - Bi(V) -universal buffer	0,31	0,32	0,32	0,32

From the obtained experimental data (Table 11) it can be seen that the maximum optical density is observed in the second order of merging of the components, therefore, for the convenience of the experiment, it was the second order of merging of the components (Bi (V) - universal buffer - TN-249) was chosen. In further studies, this order of merging of the components was used as the optimal one.

Conclusions New azo compounds synthesized by us based on pyrimidine TN-15 (2-oxo -5,6-dimethylthieno [2,3] pyrimidin-4-one) and TN-249 (2-H-5-methyl-6 -ethoxycarbonylthieno [2.3-d] pyrimidin-4-one) are the most sensitive and sufficiently selective reagents for photometric and sorption-spectroscopic determination of Bi (V).

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