

## Аналітична хімія

УДК 543.552:547.556.2

### THE USE OF SOME HETEROCYCLIC AZO DYES IN POLAROGRAPHIC ANALYSIS OF METAL IONS

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The method of linear sweep polarography was used to investigate the reduction of 4-(2-thiazolylazo)resorcinol (TAR) in the presence of Ga(III), Sc(III), In(III), Au(III), Co(II), Pd(II), Pt(IV), and Zr(IV) ions and the reduction of 4-(2-pyridylazo) resorcinol (PAR) in the presence of Au(III) and Pd(II) ions. The influence of pH, component concentration, sweep rate, on the reduction of azo dyes in the presence of metal ions was studied. Metrological and analytical characteristics of TAR-metal ions reduction were calculated. It has been established that Ga(III) and Sc(III) ions slightly affect (it was observed a potential shift in the cathodic region and a slight decrease of the reduction current) on the reduction of dye, and in the presence of Au(III), Pd(II), Zr(IV) ions the peak of the dye decreases at established pH range. In the presence of In(III), Pt(IV) ions the new cathode peaks are observed. It was found that the sensitivity of the determination is approximately the same for all investigated metals and LOQ is approximately  $10^{-6}$  M.

*Key words:* polarography, azo dyes, 4-(2-thiazolylazo)resorcinol, 4-(2-pyridylazo)resorcinol, platinum, scandium, gallium, gold.

DOI: <https://doi.org/10.30970/vch.5901.172>

The application of organic complexing reagents in voltammetric (VA) methods allows increasing the sensitivity and selectivity of metals determination. Different effects such as adsorption, kinetic and catalytic effects appeared during the reduction of metal complexes are of particular interest in the search for new possibilities in the development of highly sensitive analytical techniques. Linear sweep polarography is well suited for such studies. The advantage of this method is not only the low limit of quantitation, but the good reproducibility of the results, sufficient accuracy, and the possibility to analyze multicomponent systems as well.

Prospective reagents for VA determination of metals are azo dyes. Azo dyes with hydroxo groups in ortho positions to azo group are of special interest for VA analysis. The presence in their molecules of complexing hydroxo groups and azo group, which is reduced onto dropping mercury electrode (DME) causes the formation of sufficiently strong

electroactive complex compounds (CC) with metal ions in wide pH range. This enables the use of o-hydroxo-substituted azo dyes for direct or indirect VA metal determination and especially expands the capability of determination non-electroactive metal ions.

Nowadays the heterocyclic azo dyes have even attracted more attention for their electroactivity and ability to interact with metal cations, organic compounds and nanoparticles [1–4]. Among commercial analytical reagents – heterocyclic azo dyes – are 1-(2-pyridylazo)-2-naphthol (PAN), 4-(2-pyridylazo) resorcinol (PAR) and 4-(2-thiazolylazo)resorcinol (TAR). Generally they are used for spectrophotometric determination of a number of metal cations [5–10]. However, PAR was also utilized for VA determination of some metals [11–13]. Other application of TAR is chromatographic, electrophoretic determination of platinum and transition metals [14], and concentration of metals on sorbents modified by azoreagent [15]. However, information about its application in VA analysis and electrochemical behavior is scarce. The aim of this work was investigation of the electrochemical behavior of TAR and PAR with inorganic ions onto the DME.

Linear sweep polarographic measurements were performed utilizing certified homemade digital device equipped with personal computer and temperature-controlled three-electrode cell, volume 10 ml. A DME with a drop time of 10.8 s at an open circuit served as working electrode. A saturated calomel electrode and platinum wire electrode were used as the reference and auxiliary electrodes, respectively.

The pH of solution was measured potentiometrically using MV 870 DIGITAL-pH-MESSERÄT pH-meter.

All solutions were prepared from double distilled water. Stock solutions ( $10^{-2}$  M) of metals were prepared by dissolving the appropriate quantity of pure metal containing 99.999 % of the major substance in a mixture of conc. HCl and conc. HNO<sub>3</sub> (Sfera sim (Ukraine), cp grade). The metal's solutions were standardized using complexometry [16]. Stock solution ( $10^{-3}$  M) of TAR (CAS 2246460, Chemapol) was prepared by dissolving the given amount of reagent in aqua-ethanol mixture where ethanol content was 25 %. PAR (CAS 114159, Реахим (Russia)), was prepared by dissolving the given amount of reagent in double distilled water. The following supporting electrolytes were employed: acetic acid, sodium hydroxide, ammonia and ammonium chloride (Sfera Sim (Ukraine), cp grade).

#### *Electrochemical reduction of TAR*

TAR is reduced on DME in wide range of pH 2–10. Only one cathodic and one anodic peak are registered in the whole region of the medium acidity (Fig. 1).

Generally, pH is one of the variables that commonly and strongly influence the polarographic characteristics, and therefore it is important to investigate the effects of pH on electrochemical systems. pH influences the reduction current of TAR. Change in reduction peak of pH correlates well with changes in dye existence forms in solution as well as the change in the nature of the background electrolyte from the acetate buffer solution to the ammonia at pH 6.

The influence of pH on the peak potential parameters was investigated at  $v = 0.5$  V/s. The peak potential linearly shifts to more negative values as the pH increases at  $2.0 \leq \text{pH} \leq 10.0$  that follows the equation:  $E_p$  (V) =  $-0,0699 - 0,0598 \text{ pH}$  ( $R^2 = 0.9934$ ). This fact can be explained by preliminary protonation of the azo group, leading to a decrease in the electron density in the region of the bond between two Nitrogen atoms. This dependence indicates that there is a proton transfer in the electrode reactions and/or to the presence of differently protonated species. The slope of the relationship  $E_p$  versus pH is

59.8 mV per pH unit. It is close to the theoretical value 59 mV/pH, indicating that the number of proton and electron is equal in the electrochemical process. Based on  $an_a$  0,66 value, obtained from  $-47.7 / (E_p - E_{1/2})$ , (mV) [18] values of polarograms, and the slope obtained for  $E_p$  versus pH, the number of Hydrogen participating in the rate-determining step of the reduction process for TAR is 1.

The number of electrons, involved in the electrode process stage  $n_a$  was calculated to be 1 based on the slope of  $E_p$  versus  $\ln v$ . The result showed that this electrochemical process involved one electron transfer. In addition to the discussion of pH value, it is inferred that TAR reaction mechanism is a one electron and one proton transfer process [18].

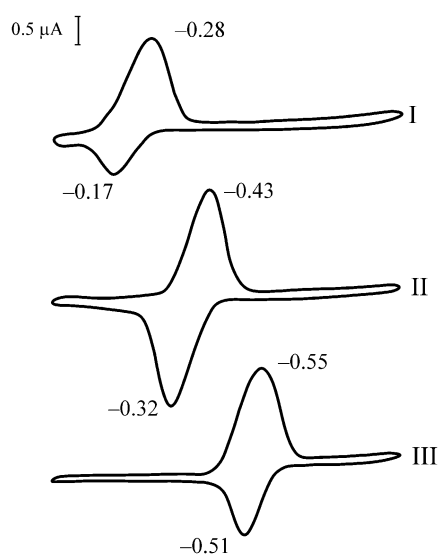


Fig. 1. Polarograms in TAR solution at pH 3.1 (I), pH 6.1 (II) and pH 8.0 (III),  $C_{\text{TAR}} = 4,0 \cdot 10^{-5} \text{ M}$ ,  $v = 0.5 \text{ V/s}$

The peak of TAR has the shape of the isosceles triangle, which is the characteristic of processes involving the adsorbed substance on the electrode surface. For the confirmation of adsorption effects contribution, the nature of the electrode process has been investigated using Semerano's criterion (criterion of rate) [19]. The logarithm of the reduction peak current of TAR is linearly dependent on the logarithm of the scan rate with a slope, which is greater than 0.5 and this result indicates that the adsorption phenomenon has effects at DME.

#### *Electrochemical reduction of TAR in the presence of metal ions*

The influence of a number of metal ions on electrochemical reduction of TAR was investigated. The studied ions belong to different groups of periodic table. However, despite different chemical properties of metal ions, for some of them there are similarities in the behaviour of TAR-metal ion on DME. Table 1 summarizes the characteristic features of TAR reduction in the presence of the studied metal ions.

When ions of metals were added to solutions of TAR, there was a change in colour. For example, in the pH range 4–6, when Ga(III) was added to the TAR solution, the colour changes from yellow to orange, and at  $\text{pH} > 8$  – from orange to red. In the presence of Eu(III), the colour changes from orange to red. Also there were changes in TAR absorption spectrum: there was a bathochromic shift of the absorption band and an increase in optical density. These changes are the signs of complexation between metal ions and TAR.

The changes in TAR spectrum and colour of solution are the results of giving oxygen and nitrogen atoms' undivided pair of electrons involved into conjugated double bonds responsible for energy absorption to metal as complexing agent [20].

Table 1

Peculiarities of TAR reduction in the presence of different metal ions

Metal ion	pH	Effect of metal ion on TAR reduction	Additional information
Ga(III)	4.0; 8.0		With increasing concentration of M(III), the height of the TAR reduction peak decreases to some extent, but the decrease is observed in the narrow limits of the concentrations (from the ratio of TAR: M(III) = 1: 0.25 to 1: 1)
Sc(III)	6.0–8.0	Shift of $E_{TAR}$ in the cathodic region and a slight decrease of $I_{TAR}$	
Eu(III)	4.0–9.0		–
Pd(II)	2.5–7.5	Decrease of $I_{TAR}$	–
Au(III)	4.0–6.0	Decrease of $I_{TAR}$ . The largest decrease (8 times) is observed at pH 5	During storage of TAR-Au(III) solutions for a long time (day), an orange precipitate appears, which dissolves when stirring. It does not significantly affect the polarographic characteristics. In ethanol, the precipitate does not appear, but in the alcohol medium, the current of the TAR cathodic peak in the presence of Au(III) decreases only by 1.5 times
Zr(IV)	5.0–7.0	Slight shift of $E_{TAR}$ in the cathodic region and a decrease of $I_{TAR}$	The height of TAR reduction peak linearly decreases with increase in the concentration of Zr(IV)
Co(II)	6.0–7.0 ≥ 8.0	Peak of TAR becomes broader Increase of $I_{TAR}$	The broader the peak of TAR may be the result of appearance of an additional peak of complex Co(II)-TAR that is overlapped with dye's peak
Pt(IV)	2.5–7.5 8.0	Increase of $I_{TAR}$ Appearance of new reduction peak	With an increase in the concentration of Pt(IV), the peak height of TAR reduction and the new peak increases
In(III)	6.0–9.0	Appearance of new reduction peak of In(III)	With an increase in the concentration of In(III), the peak height of new peak increases

However, changes observed in polarograms of TAR in the presence of Ga(III), Sc(III), REE(III), Au(III), Pd(II) and Co(II) ions are negligible (Table 1). There were no additional peaks that would correspond to the reduction of CC. Thus the observed effects with these metals can not be used for analytical purposes.

Zr(IV) causes changes in polarographic characteristic of TAR reduction similar to metal ions mentioned above (Table 1). However, the height of TAR reduction peak linearly decreases with increase in the concentration of Zr(IV) (Fig. 2). Metrological characteristics of Zr(IV) determination by polarography are given in Table 2. Unfortunately, the methods based on decreasing the currents of reduction peaks are not selective, so the research with Zr(IV) was not continued.

The new peaks were registered only in the presence of Pt(IV) and In(III). In the presence of Pt(IV) an additional reduction peak appeared only at pH 8,0 at a potential  $-0.28$  V. An example of polarograms is shown in Fig. 2. At lower pH 2.5–7.5 Pt(IV) caused increase of TAR reduction peak and no new peaks were registered.

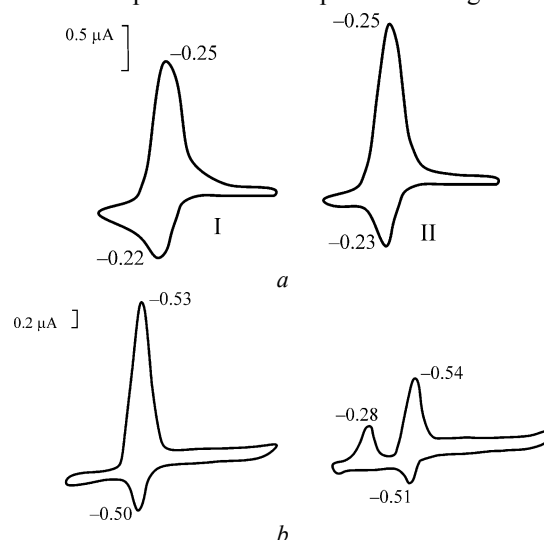


Fig. 2. Polarograms of TAR in the absence of Pt(IV) (I) and in the presence of Pt (IV) (II) at pH 3.0 (a), pH 8,0 (b);  $C_{\text{TAR}} = 4.0 \cdot 10^{-5}$  M,  $C_{\text{Pt(IV)}} = 2.0 \cdot 10^{-5}$  M,  $v = 0.5$  V/s

As the concentration of Pt(IV) increases, the height of TAR reduction peak and the new peak increases somewhat (Table 2), but the sensitivity and selectivity of such determination are insufficient for use in the analysis.

When ions of In(III) are added to the TAR solution in the range of pH 6.0–9.0, a new peak of metal reduction appears at a potential ( $-0.72 - -0.75$ ) V (Fig. 3). Within the pH range 6.0–9.0, the ions of In(III) are not reduced at the background of indifferent electrolytes. As the concentration of metal increases, the current of the TAR reduction peak remains unchanged, and the current of additional peak increases. Complex formation in this system is not occurred. The appearance of an additional peak of In(III) reduction can be explained by the “bridge effect”. Therefore, an increase in the rate of the charge transfer reaction is a result of changes in the double electric layer in the presence of an adsorbed anions of azo dye on the surface of the electrode. It is known that the electron transfer rate is determined by the effective potential jump between the electrode  $\phi_a$  and the center of the electroactive particles in the Helmholtz plane, that is, the value of  $\phi_a - \phi_1$  ( $\phi_1$  is the potential in the Helmholtz plane). In the presence of cations adsorbed on the electrode, the potential  $\phi_1$  decreases, and an acceleration of the anion reduction process is observed [21].

In the case of the reduction of In (III) in the presence of TAR, the anions of the dye are adsorbed on the surface of the electrode. Obviously this is due to the growth of the negative  $\phi_1$  potential and, consequently, the increase of the effective potential jump, resulting in increase of the cathode electrode process rate with the participation of cations of In(III). This effect of increasing the current of metal ions reduction in the presence of adsorbed substances on the electrode surface is called “bridge effect”. Therefore, the peak  $P_2$  at the potential  $-0.75$  V corresponds to the reduction of In(III) ions.

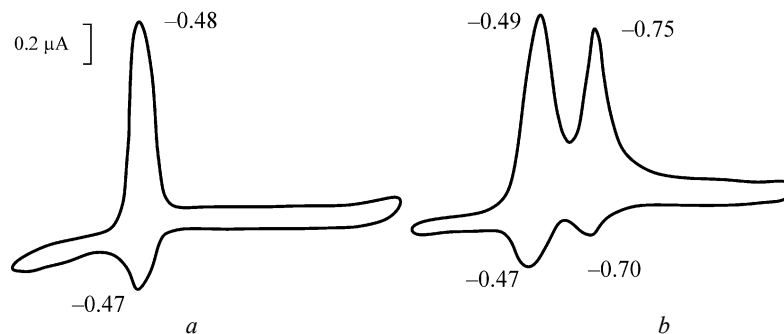


Fig. 3. Polarograms of TAR in the absence of In(III) (a) and in the presence of In(III) (b) at pH 7.5,  $C_{\text{TAR}} = 4.0 \cdot 10^{-5}$  M,  $C_{\text{In(III)}} = 2.0 \cdot 10^{-5}$  M,  $v = 0.5$  V/s

At pH 7.5, the influence of the concentration of In(III) on the polarogram in the solutions of TAR-In (III) was investigated. As the concentration of In (III) increases, the current of the new reduction peak at -0.75 V increases.

A linear increase in the peak current at -0.75 V with an increase in the concentration of In(III) in the solution in the presence of TAR (pH 7.5) is registered within the concentration of  $1 \cdot 10^{-6}$ – $1 \cdot 10^{-5}$  M. Metrological characteristics of the determination of In(III) using TAR are given in Table 2.

#### *Electrochemical reduction of PAR in the presence of metal ions*

Despite the similarity of PAR and TAR structure, their reduction on DME is different.

PAR is reduced in a wide range of pH 2–10 on DME. At pH 4–5 and pH 9–10, two cathodic peaks are observed on the polarograms, while at pH 2–3 and 6–8, there is only one cathodic peak [11].

With increasing pH, the potentials of the cathodic peaks of PAR reduction are linearly shifted toward negative potentials, and the current changes. The change in the current correlates with the dye's existence forms.

The charge transfer rate during reduction of PAR is higher than during reduction of TAR, as evidenced by significantly higher reduction currents measured under the same conditions.

On polarograms in the solution of PAR in the presence of Au(III) ions, the decrease of dye's reduction peaks currents was observed in the pH range 3.5–5.0; no additional peaks were registered.

When ions Pd(II) were added to the solution of PAR, a change of colour from yellow to green was observed at  $\text{pH} < 4$  and from yellow to red at  $\text{pH} \geq 5$ . At pH 5, in the presence of Pd (II) in the solution of PAR, we observed the appearance of a new peak shifted in anodic region towards dye's peaks and decrease of the dye's reduction peak (Fig. 4). As the concentration of Pd(II) increases, the new peak increases, but the sensitivity and selectivity of such a determination is insufficient for use in the analysis.

In the alkaline medium, a new peak, corresponding to the reduction of amminepalladium (II) complex, was observed.

Table 2

Metrological characteristics of the determination of metal ions with the use of TAR,  $C_{TAR}=4 \times 10^{-5}$  M

Characteristic	Linear range	Equation	$C_{in}$ , M	$\Delta a$	$\Delta b$	$S_r$	R
Zr(IV). pH 6,0 $E = -0.49$ V	$1 \cdot 10^{-6} - 1 \cdot 10^{-5}$	$I = 0.18 + 3.36 \cdot 10^4 \cdot C$	$1.00 \cdot 10^{-6}$	$2.0 \cdot 10^{-2}$	$2.0 \cdot 10^3$	$3.78 \cdot 10^{-2}$	0.9995
Pt(IV). pH 8,0 $E = -0.28$ V	$1 \cdot 10^{-6} - 1 \cdot 10^{-5}$	$I = 0.37 + 1.83 \cdot 10^4 \cdot C$	$1.08 \cdot 10^{-5}$	$1.8 \cdot 10^{-1}$	$6.4 \cdot 10^3$	$3.98 \cdot 10^{-2}$	0.9935
Pt(IV). pH 8,0 $E = -0.54$ V	$1 \cdot 10^{-6} - 1 \cdot 10^{-5}$	$I = 1.03 + 1.11 \cdot 10^4 \cdot C$	$7.19 \cdot 10^{-6}$	$6.1 \cdot 10^{-2}$	$1.3 \cdot 10^4$	$3.86 \cdot 10^{-2}$	0.9788
In(III). pH 7.5. $E = -0.75$ V	$1 \cdot 10^{-6} - 1 \cdot 10^{-5}$	$I = 0.28 + 5.3 \cdot 10^4 \cdot C$	$1.98 \cdot 10^{-6}$	$7.0 \cdot 10^{-2}$	$1.1 \cdot 10^4$	$2.60 \cdot 10^{-2}$	0.9938

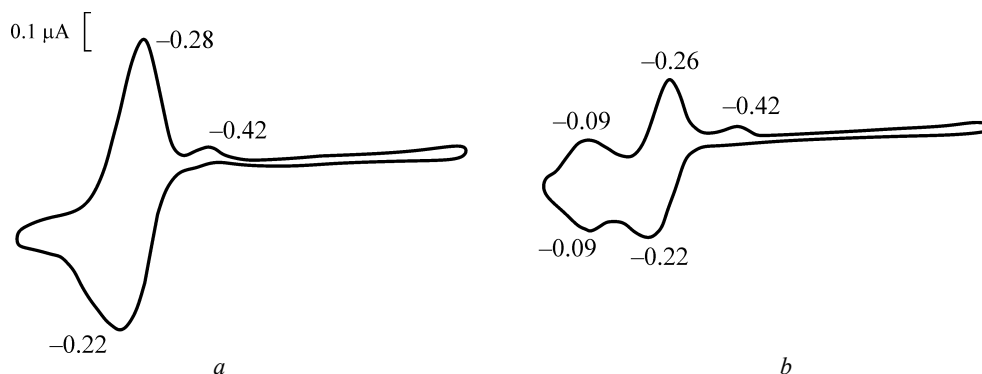


Fig. 4. Polarograms of PAR in the absence of Pd(II) (a) and in the presence of Pd (II) (b) at pH 5.0,  $C_{\text{PAR}} = 4.0 \cdot 10^{-5}$  M,  $C_{\text{Pd(II)}} = 2.0 \cdot 10^{-5}$  M,  $\nu = 0.5$  V/s

It was established that TAR is reduced on DME in pH range 2–10 using linear sweep polarography. Only one cathodic peak was registered.

Ga(III), In(III), Sc(III), REE(III), Co(II) and Pd(II) ions form complexes with PAR and TAR, which is confirmed by changes in azo dyes' absorption spectra and colour in the presence of ions of metal. However, substantial changes in polarographic characteristics of studied dyes were observed not for all investigated metal ions.

Observed changes in polarograms of PAR and TAR in the presence of Ga(III), Sc(III), Zr (IV), Co(II) Au(III), Pd(II) are not substantial and cannot be used for analytical purposes.

New peaks were observed only for In(III) and Pt(IV) ions. On polarograms of TAR at pH 8 in the presence of ions Pt(IV) there is an additional peak corresponding to the reduction of CC Pt(IV)–TAR. The height of this peak increases with increasing of Pt (IV) concentration. Linearity  $I$ ,  $\mu\text{A}$  from  $C_{\text{Pt(IV)}}$  is in the range  $1 \cdot 10^{-6}$  M to  $1 \cdot 10^{-5}$  M.

In the presence of In(III) ions within pH 6–8, additional peak appeared on the polarograms that correspond to the reduction of the ions of In (III) due to the "bridge effect". The height of this peak increases with an increase in the concentration of In(III). Linearity  $I$ ,  $\mu\text{A}$  from  $C_{\text{In(III)}}$ , M is in the range from  $1 \cdot 10^{-6}$  M to  $1 \cdot 10^{-5}$  M.

The systems Pt(IV)–TAR and In(III)–TAR can be used as analytical forms for the further development of a polarographic method for determination of these metal ions.

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### ВИКОРИСТАННЯ ДЕЯКИХ АЗОБАРВНИКІВ НА ОСНОВІ ГЕТЕРОЦИКЛІВ У ПОЛЯРОГРАФІЧНОМУ АНАЛІЗІ ІОНІВ МЕТАЛІВ

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Стаття містить стислий огляд про використання азобарвників на основі гетероциклів у вольтамперометричному аналізі. Експериментально методом полярографії зі швидкою лінійною розгорткою дослідили відновлення 4-(2-тіазолілазо)-резорцину (ТАР) за наявності іонів Ga(III), Sc(III), In(III), Au(III), Co(II), Pd(II), Pt(IV) і Zr(IV), а також 4-(2-піридилазо)-резорцину (ПАР) за наявності іонів Au(III) та Pd(II) в широких межах рН і концентрації реагентів. Азобарвник ТАР відновлюється на ртутному краплинному електроді квазіоборотно в одну стадію (з утворенням одного катодного й одного анодного піків) у широких межах рН від 2 до 10. Визначено, що додавання розчинів, які містять іони металів, до розчинів азобарвників зумовлює зміну забарвлення і батохромний зсув молекулярної смуги поглинання барвників. Наприклад, за рН 4–6 за наявності Ga(III) забарвлення розчину ТАР змінюється з жовтого на оранжеве. Однак іони Ga(III) та Sc(III) мало впливають на відновлення барвника (простежується зсув потенціалу піка відновлення органічного реагента в катодну ділянку та незначне зменшення струму), а за наявності іонів Au(III), Pd(II) і Zr(IV) пік барвника зменшується за визначеного діапазону рН. Наявність у розчині ТАР іонів Co(II) зумовлює розширення піка відновлення азобарвника і збільшення струму, що, очевидно, пов'язано з відновленням комплексної сполуки Co(II) з ТАР за близьких потенціалів. За наявності іонів Pt(IV) та In(III) простежуються нові катодні піки. Зокрема, доведено, що пік за наявності In(III) зумовлений “містковим ефектом”. Розраховано метрологічні характеристики полярографічного визначення іонів металів за посередництвом ТАР. З'ясовано, що межа визначення є приблизно однакова для всіх досліджених іонів металів і становить приблизно  $10^{-6}$  М.

*Ключові слова:* полярографія, азобарвники, 4-(2-тіазолілазо)-резорцин, 4-(2-піридилазо)-резорцин, Платина, Скандій, Галій, Аурум.

Стаття надійшла до редколегії 31.10.2017

Прийнята до друку 11.04.2018