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ARTICLES

A Gallium Arsenide Sensor for the Potentiometric Titration of Silver, Copper, Lead, and Cadmium Ions

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Abstract—Semiconductor sensors based on gallium arsenide, modified by the electrochemical method, have been developed for the potentiometric titration of metal ions. After surface modification, the electroanalytical characteristics of GaAs electrodes are improved, namely, the slope of the electrode function increases, the linearity range of the electrode function widens, and the response time decreases.

Keywords: semiconductor sensors, gallium arsenide, electrode function, ions of silver, copper, lead, and cadmium

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Potentiometric titration with ion-selective electrodes is widely used for the analysis of various samples because of their cost-effectiveness, simplicity, and portability. The creation of new indicator electrodes and the improvement of already known ones are among the urgent tasks of potentiometric analysis. Semiconductor electrodes are often used for the analysis of liquid media; they have many advantages: availability, stability in aggressive media, mechanical strength, and long service life.

Surface modification is often used to improve the electroanalytical properties of indicator electrodes. Recently, modified electrodes have found wider application in electroanalytical practice. Surface modification adds new properties to indicator electrodes, in addition to conventional ones, which increase their reactivity and selectivity [1].

Many publications were devoted to methods for the targeted modification of the surface of ion-selective electrodes (ISEs), metal or semiconductor, and their use in potentiometric analysis. For example, Kulapina et al. [2] proved a possibility of modifying the surface of surfactant-sensitive sensors with polyvinyl chloride monomolecular sieves with different pore sizes. The potentiometric selectivity coefficient for modified electrodes decreases by three to four orders of magnitude, which indicates a possibility of the separate determination of surfactants.

Kiyanskii [3] proposed the modification of the surface of chalcogenide electrodes by changing its chemical, electrochemical, or mechanical properties. It was found that, for chalcogenide sensors, a change in the function in solutions of interfering metal cations is associated with the occurrence of solid-phase reactions leading to the formation of less soluble compounds in the electrode-active layer. On keeping silver-sulfide membranes in solutions of mercury(II) chloride, they acquire both mercury and chloride functions.

Unmodified and modified $A^{III}B^{V}$ semiconductor electrodes in solutions of metal salts, halides, and complexing agents were developed and their properties were studied in [4]. The proposed electrodes are suitable as indicators in acid–base, precipitation, complexometric, and potentiometric titration.

In [5], semiconductor electrodes based on gallium arsenide (GaAs) were studied, and a possibility of their use as indicator electrodes in various versions of potentiometric titration was shown. The proposed modification of the semiconductor surface of a GaAs electrode by an electrochemical method improved the electrode function, operation range, response time, and reproducibility.

Thus, the study of the electrode properties of solid semiconductor gallium arsenide electrodes in solutions of metal salts and their use in potentiometric titration is relevant. Earlier, we studied the electroanalytical characteristics of a GaAs electrode in solutions of silver ions and halides.

The goal of this work was to study patterns of functioning of electrochemically modified electrodes based on semiconductor materials from gallium arse-

Table 1. Analytical properties of modified sensors with a GaAs membrane in 0.1 M Na_2S and $AgNO_3$ solutions

Characteristics	Modification time		
	3 min	5 min	10 min
E, mV	−175	−170	−170
Linearity range of the electrode function $E = f(pc_{Ag+})$ (M)	10^{-5}–0.1 M	10^{-5}–0.1 M	10^{-5}–0.1 M
Slope of the electrode function, mV/pc_{Ag+}	65 ± 2	66 ± 2	66 ± 2

nide (GaAs) in solutions of silver, copper, lead, and cadmium salts.

EXPERIMENTAL

We used electrodes based on semiconductor materials from gallium arsenide (GaAs) as electrochemical sensors for potentiometric studies. To manufacture the sensors, single-crystal $A^{III}B^{V}$ semiconductor materials—gallium arsenide—were used as electrode-active membranes. Disks 5–6 mm in diameter and 2.0 ± 0.5 mm in thickness were cut from the prepared semiconductor materials and glued to the electrode body with an epoxy compound. The internal down conductor was made based on the “solid–solid” principle, characteristic of noncontact type electrodes. The wire was attached to the inner side of the membrane using a conductive contact film made of an epoxy compound and fine silver powder. The electrode case was made of an inert polymer material. A port for connecting to the measuring device was soldered to the end of the conductor.

The membrane surface of the GaAs sensor was preliminarily renewed by machining with fine sandpaper, then it was thoroughly washed with distilled water and dried with filter paper. Between measurements, the sensor was stored dry.

Solid-state ion-selective electrodes were also used as indicator electrodes: ESL-43-07 glass electrodes (Belarus); a copper-selective electrode (Cu-SE) with an Ag_2S–CuS membrane, a lead-selective electrode (Pb-SE) with an Ag_2S–PbS membrane, and a cadmium selective electrode (Cd-SE) with an Ag_2S–CdS membrane, produced in the Laboratory of Chemical Sensors of the St. Petersburg State University and at the Research Institute of the Western Kazakhstan Agrarian and Technical University.

In this work, we used a universal Anion-4100 potentiometer in the millivoltmeter mode (EMF measurement error was ±0.01 mV). The electrochemical cell consisted of a GaAs electrode and an EVL-1MZ silver–silver chloride reference electrode filled with a saturated potassium chloride solution. The solutions were stirred with a magnetic stirrer.

The surface of the GaAs electrode was modified by electrochemical treatment in solutions of sodium sulfide and silver nitrate; the treatment time was varied. modification was performed in the mode U = 20–25 V, I = 0.05 A, using a VUP-2M current rectifier.

The time of electrode treatment in modifier solutions was varied. It was 3, 5, and 10 min. The results obtained after the electrochemical modification of an electrode with a GaAs membrane with $AgNO_3$ solutions, depending on the time of modification and the concentration of the modifying solution, are presented in Table 1. The best results were obtained by storing the membrane of the studied electrodes in a 0.1 M $AgNO_3$ solution, because in using more dilute solutions, the initial characteristics of the electrodes did not change. The recommended time for electrochemical modification, sufficient for obtaining optimal electrode characteristics, was 5 min. In this case, the electrode acquired a stable electrode function to Ag^+ ions in the concentration range from 10^{-5} to 0.1 M with a slope of 66 ± 2 mV/pc_{Ag+}.

To compare the results and take into account reproducibility, the determination was carried out repeatedly; the results were processed statistically. The response time was fixed by a stopwatch 1 min after the immersion of the electrodes into the solution. The pH of the solution was controlled with a glass electrode. All measurements were carried out at 25 ± 1°C. In the transition from one metal to another in the potentiometric titration, the surface of the semiconductor sensor was renewed with sandpaper, after which the function of the electrode to the detected ion remained well reproducible.

RESULTS AND DISCUSSION

We studied the electroanalytical properties of potentiometric sensors based on semiconductor material from gallium arsenide before and after the electrochemical modification of their surfaces in solutions of metal salts. After the electrochemical surface treatment, the functions of gallium arsenide electrodes were noticeably improved because of reactions occurring on the membrane surface, which led to the appearance of a thin modified layer. In some cases, an extension of the linearity range, an increase in the slope of the electrode function, and a decrease in response time were observed.

To study the electroanalytical characteristics of unmodified and modified GaAs electrodes (slope of the electrode function, linearity range of the function, response time, reproducibility), their behavior in solutions of copper, lead, and cadmium ions was studied. Conventional Ag-SE, Cu-SE, Pb-SE, and Cd-SE were taken as standard electrodes.

We assessed the behavior of the GaAs electrode in solutions of silver salts. It was found that GaAs electrodes are most sensitive to silver ions. A comparison of the data on unmodified and modified GaAs electrodes showed that the E–pc dependence was linear in the concentration range from 10^{-5} to 0.1 M for both electrodes. However, they differed in the slope of the electrode function: for modified GaAs electrodes, $S = 66 \pm 2$ mV/p$c_{\mathrm{Ag+}}$, while before modification, it was $S = 56 \pm 2$ mV/p$c_{\mathrm{Ag+}}$. After treating the surface of the membranes, the concentration dependence of the potential for the GaAs electrode shifted to the range of potentials characteristic of the silver-selective electrode (Ag-SE). The response time did not exceed 15–20 s.

We studied the behavior of the GaAs electrode in solutions of copper salts. The best results were obtained after the surface treatment of the membranes. The slope of the electrode function of the GaAs electrode after modification was 28 ± 2 mV, while before the modification, it was 20 ± 2 mV. The surface treatment of the GaAs electrode improved the limit of detection by an order of magnitude, from 10^{-5} to 10^{-6} M. For the sensor with a modified surface, the response time shortened almost threefold, from 60 s to 15–20 s. After the sequential electrochemical treatment of the surface of the GaAs electrode with 0.1 M solutions of Na_2S and $Cu(NO_3)_2$, the calibration curve shifted to the region of positive potentials characteristic of the copper selective electrode (Cu-SE). This indicates the occurrence of solid-phase reactions on the surface of the GaAs electrode with the formation of a film of insoluble copper sulfide, because of which the GaAs electrode functioned as a Cu-SE.

Similar results were obtained in studying the electrode potential–concentration dependence for the GaAs electrode in solutions of lead ions before and after the modification of its surface. It was found that the electrochemical modification of the membrane surface led to an improvement in the analytical characteristics of the electrode. The GaAs electrode, alternately treated with 0.1 M Na_2S and $Pb(NO_3)_2$ solutions for 5 min, had a Pb^{2+} function in the range from 10^{-6} to 0.1 M with a slope of the electrode function of 25 ± 2 mV, whereas, for an unmodified electrode, it was 22 ± 2 mV. The response time was reduced to 15–20 s, compared to 60 s for an unmodified electrode. The electrochemical modification of the GaAs electrode resulted in a shift in the calibration curves to the region of positive potentials, which is typical for chalcogenide electrodes.

Studies of the dependence of the potentials of unmodified and modified GaAs electrodes on the concentration of cadmium ions have shown that the best results were obtained after the surface treatment of the membranes. The electrochemical activation of a GaAs electrode with 0.1 M solutions of Na_2S and $Cd(NO_3)_2$ for 5 min improved the characteristics of the electrode: the slope of the electrode function became 22 ± 2 mV, while before modification, it was 18 ± 2 mV. The concentration range extended to 10^{-5} M, and the response time for a GaAs electrode with a treated surface decreased threefold. For the modified GaAs electrode, we observed a shift of the calibration curve to the range of potentials characteristic of the cadmium selective electrode. The electrochemical treatment resulted in the formation of a modified layer on the membrane surface, and subsequently, the electrode functioned as an electrode of the first kind.

The results of the experiment are presented in Table 2. It can be seen that, for modified GaAs electrodes, the electroanalytical characteristics are improved compared to the unmodified electrodes: the slope of the electrode function increases, the linearity range of the E–pc function extends, and the response time decreases.

Thus, the electrochemical modification method is effective in the surface treatment of membranes. After electrochemical surface treatment, the functions of GaAs electrodes have been improved because of reactions occurring on the membrane surface and leading to the formation of a sulfide layer.

Electrochemical reactions occur at the semiconductor–electrolyte solution interface; they are responsible for the appearance of the semiconductor electrode potential. We can distinguish between the anodic reaction, associated with the oxidation (corrosion, dissolution) of the semiconductor, and cathodic reactions, proceeding with the reduction of the dissolved oxidant.

When the electrodes are immersed in solutions of metal salts, metal ions are reduced to the metallic state on the cathodic surface areas, that is,

$$\mathrm{Me}^{n+} + \bar{e} \rightarrow \mathrm{Me}^{(n-1)+} \quad \text{or} \quad \mathrm{Me}^{n+} + n\bar{e} \rightarrow \mathrm{Me}^{0}.$$

Our data showed that the value of the GaAs electrode potential depends on the concentration of silver, copper, lead, and cadmium ions. A correlation was found between the sensitivity of GaAs electrodes to the ions of these metals and the values of standard electrode potentials. The more positive the standard redox potential of the adsorbed metal, the more the shift of the semiconductor electrode potential to the positive region. This also affects the slope of the electrode function in solutions of metal salts. The GaAs electrode exhibits the highest sensitivity to silver ions

Table 2. Electroanalytical properties of unmodified and modified GaAs electrodes in solutions of silver, copper, lead, and cadmium nitrates

Ion	Electrode	Linearity range of the electrode function $E = f(c_i)$ (M)	Slope of the electrode function, mV/pc	Response time, s
Ag^+	GaAs (nonmod.)	10^{-5}–0.1	56 ± 2	60–90
	GaAs (mod.)	10^{-5}–0.1	66 ± 1	15–20
	Ag-SE	10^{-6}–0.1	59 ± 2	20–30
Cu^{2+}	GaAs (nonmod.)	10^{-5}–0.1	20 ± 5	60–90
	GaAs (mod.)	10^{-6}–0.1	28 ± 1	15–20
	Cu-SE	10^{-6}–0.1	29 ± 2	20–30
Pb^{2+}	GaAs (nonmod.)	10^{-5}–0.1	22 ± 5	60–90
	GaAs (mod.)	10^{-6}–0.1	25 ± 1	15–20
	Pb-SE	10^{-5}–0.1	29 ± 2	20–30
Cd^{2+}	GaAs (nonmod.)	10^{-4}–0.1	18 ± 5	60–90
	GaAs (mod.)	10^{-5}–0.1	22 ± 1	15–20
	Cd-SE	10^{-5}–0.1	29 ± 2	20–30

($E^0_{Ag^+/Ag^0} = 0.799$ V) and the least sensitivity to cadmium ions ($E^0_{Cd^{2+}/Cd^0} = -0.403$ V).

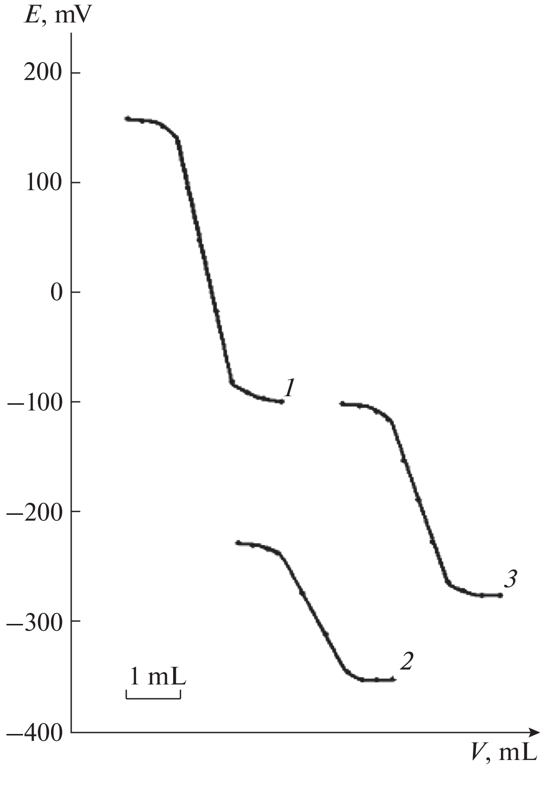

Fig. 1. Curves of potentiometric titration of silver ions with a 0.01 M Na_2S solution with (*1*) Ag-SE and GaAs electrodes (*2*) before modification and (*3*) after modification.

Thus, the sensitivity of the semiconductor GaAs electrode in metal salt solutions can be explained by the occurrence of redox reactions on the electrode surface, leading to the formation of a surface layer and the specific adsorption of oxidant ions, that is, the reduction of the adsorbed ions to a metallic state on the electrode surface [6].

The presence of a response of the studied electrodes to Ag, Cu, Pb, and Cd ions is confirmed by the curves of their potentiometric titration with a 0.01 M Na_2S solution. Figures 1–4 show the potentiometric titration curves of solutions of Ag, Cu, Pb, and Cd nitrates with a 0.01 M Na_2S solution using unmodified and modified GaAs electrodes.

The curves of potentiometric titration of a 0.01 M $AgNO_3$ solution with sodium sulfide solutions are shown in Fig. 1. The modified GaAs electrodes yield sharper potential jumps of larger magnitude (Fig. 1, curve *3*) compared to unmodified electrodes (Fig. 1, curve *2*). The potential jump at the titration endpoint with an unmodified GaAs electrode was 105 mV; after surface modification, it was 145 mV. The potentiometric titration curve after the surface treatment of the GaAs electrode shifted to the region of the functioning of the Ag-SE (Fig. 1, curve *1*). The response time at the titration endpoint did not exceed 10 s.

Similar results were obtained for the potentiometric titration of copper ions with a 0.01 M Na_2S solution. Using modified GaAs electrodes, the titration curves were obtained with potential jumps of larger magnitude, shifted to a more positive range of potentials (Fig. 2). The potential jump with a modified GaAs electrode was 135 mV (Fig. 2, curve *3*), and with an unmodified one, it was 100 mV (Fig. 2, curve *2*).

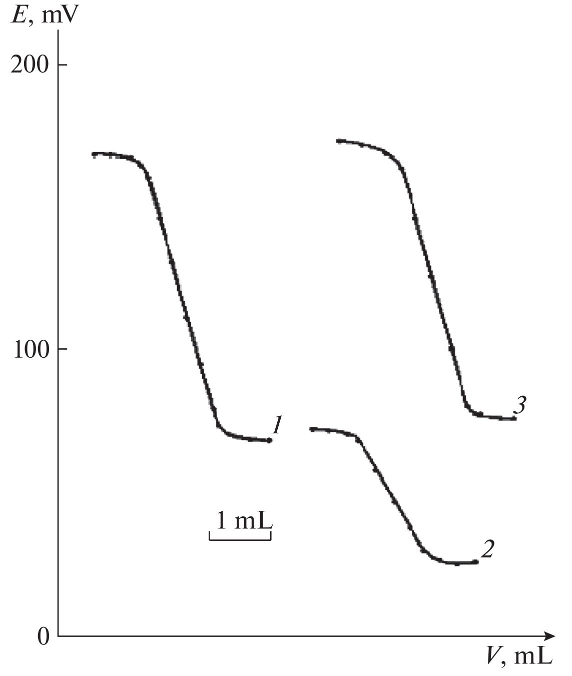

Fig. 2. Curves of potentiometric titration of copper ions with a 0.01 M Na_2S solution using (*1*) Cu-SE and GaAs electrodes (*2*) before modification and (*3*) after modification.

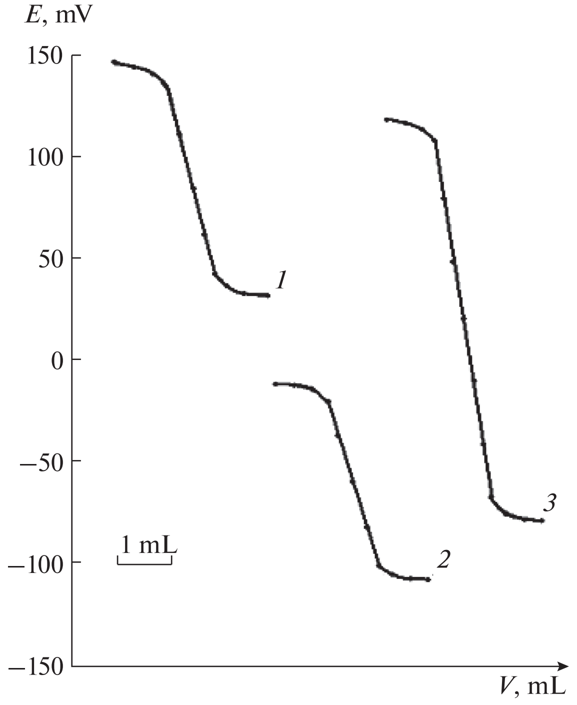

Fig. 3. Curves of potentiometric titration of lead ions with a 0.01 M Na_2S solution using (*1*) Pb-SE and GaAs electrodes (*2*) before modification and (*3*) after modification.

The experimental results correlate well with the data of direct potentiometry. The response time was halved in the case of modified GaAs electrodes.

In the potentiometric titration of lead ions with a 0.01 M solution of Na_2S using GaAs electrodes, the best results were obtained with a modified electrode. The potential jump for the unmodified GaAs electrode was 90 mV (Fig. 3, curve *2*), and for those sequentially modified with 0.1 M solutions of Na_2S and $Pb(NO_3)_2$, the potential jump was 110 mV (Fig. 3, curve *3*). The potential value at the unmodified electrode was stabilized for 60 s, and after modification of the electrode surface, the potential reached immediately its stable value.

We compared the characteristics of unmodified and modified GaAs electrodes in solutions of cadmium ions. It was found that the electrodes with a modified membrane surface gave sharper and more reproducible titration curves (Fig. 4, curve *3*). The potential jump for the unmodified GaAs electrode was 30 mV (Fig. 4, curve *2*), and for the modified electrode, it increased two times and amounted to 60 mV (Fig. 4, curve *3*). The steady-state value of the potential was reached within 10 s after the addition of the next portion of the titrant. At the titration endpoint, the equilibrium potential was reached instantly.

Thus, the proposed modification of the surface of GaAs semiconductor electrodes by the electrochemical method leads to an increase in the potential jump and a decrease in response time, which ensures the more accurate and reliable detection of the titration endpoint.

The results of the determination of copper ions by potentiometric titration with a Na_2S solution using a modified GaAs electrode are shown in Table 3. The accuracy of the results was evaluated by the standard addition method.

The potentiometric titration of Cu^{2+} in model solutions using GaAs electrodes is characterized by sufficient accuracy and good reproducibility.

We studied a possibility of using electrochemically modified GaAs electrodes as indicator electrodes for determining sulfide ions in the gas condensate of the Karachaganak oil and gas condensate field in the Western Kazakhstan region. The determination of sulfides is critical for solving the environmental problems of the Western Kazakhstan, rich in hydrocarbon raw

Table 3. Results (mg) of the potentiometric titration of copper ions with a 0.01 M Na_2S solution using a modified GaAs electrode ($n = 4$, $P = 0.95$)

Added	Found, $c \pm \delta$	RSD, %	δ, %
2.13	2.11 ± 0.03	0.05	2
3.20	3.26 ± 0.06	0.03	6
6.40	6.5 ± 0.1	0.04	14

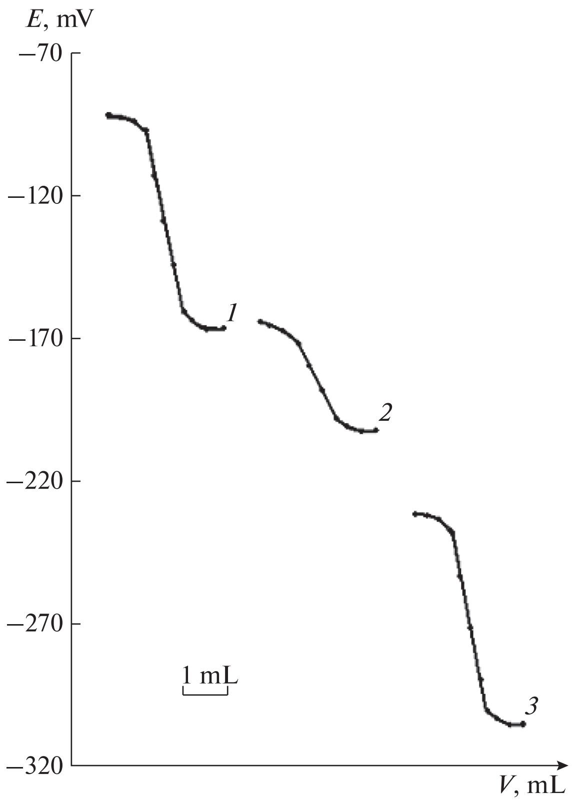

Fig. 4. Curves of potentiometric titration of cadmium ions with a 0.01 M Na_2S solution using (*1*) Cd-SE and GaAs electrodes (*2*) before modification and (*3*) after modification.

Table 4. Results (%) of the determination of mercaptans in a gas condensate with (I) a sulfide selective electrode and (II) unmodified and (III) modified GaAs electrodes ($n = 4$, $P = 0.95$)

Sample	I	II	III
1	0.29 ± 0.01	0.27 ± 0.01	0.28 ± 0.02
2	0.37 ± 0.01	0.35 ± 0.01	0.36 ± 0.02

materials with a high concentration of sulfur compounds.

Sulfide ions were determined by the deposition method using a 0.1 M $AgNO_3$ solution as a titrant. The results of titration of the gas condensate of the Karachaganak oil and gas condensate field with sulfide-selective and GaAs electrodes are compared in Table 4. The results obtained using the conventional sulfide-selective electrode and the modified GaAs electrodes are characterized by good convergence. It can be concluded that electrochemically modified GaAs semiconductor electrodes enable the determination of mercaptans with high accuracy and good reproducibility. These electrodes have long service life (more than 10 years), mechanical strength, and resistance in aggressive sulfur-containing media. The GaAs electrode was also used in analytical, environmental, and petrochemical laboratories in the study of various samples, and it showed high reliability in performing routine analyzes.

CONCLUSIONS

Thus, we demonstrated a possibility of using sensors based on $A^{III}B^{V}$ semiconductor compounds (gallium arsenide) for potentiometric titration. The sensitivity of the proposed electrode to cations makes it promising for the environmental monitoring of natural samples and rapid quality control of various products.

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