Determination of Zinc Ion by Inversion Voltammetric Method from the Composition of Wastewater Using an Electrochemical Sensor

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Abstract In this study, advanced techniques for the precise detection of zinc ions in minute quantities within wastewater samples have been innovatively developed through the customization of electrochemical sensors using the inversion-voltammetric method. This research not only presents the novel methodologies established for the efficient identification of zinc ions but also focuses on enhancing the metrological characteristics associated with zinc ion determination through the inversion-voltammetric approach. By refining the assessment protocols and methodologies, this study contributes significantly to the field of analytical chemistry, paving the way for more accurate and reliable monitoring of zinc ion levels in wastewater, thereby facilitating improved environmental management practices and ensuring the protection of public health.

Keywords Microelement, Wastewater, Zinc, Background electrolyte, Stripping voltammetry, Adjacent cations, Electrochemical sensor, Trace element, Side cations, Buffer mixture

1. Introduction

Today, the relentless growth in people's demand for industry, economy, food, and various products is a prevailing trend, exacerbating the volume of wastes discharged into the environment, notably wastewater [1-2]. The detrimental impact on flora and fauna stemming from these environmental emissions is intensifying at an alarming rate, underscoring the pressing need for contemporary analysts to devise increasingly precise and effective methodologies. This imperative arises from several critical factors: firstly, the imperative to oversee and regulate product quality to align with contemporary standards; secondly, the essential task of averting environmental degradation caused by waste products generated in the production processes; and thirdly, the urgent issue of escalating levels of heavy metals in wastewater, posing a direct threat to human health.

The surge in heavy metal concentrations within wastewater presents a multifaceted challenge, necessitating immediate attention to mitigate its adverse consequences on both environmental ecosystems and public well-being. Of particular concern is the link between industrial and economic activities and the contamination of wastewater with heavy metals, which in turn contributes to the proliferation of severe illnesses and health hazards among populations exposed to such pollutants.

In essence, the escalating demands of our modern society underscore the critical importance of implementing innovative strategies and sustainable practices to curb environmental degradation and foster a more harmonious coexistence between human activities and the natural world. By promoting responsible resource management, fostering interdisciplinary collaboration, and championing advancements in environmental stewardship, we can strive towards a cleaner, healthier, and more sustainable future for all.

Considering the formidable challenges outlined above, the focal point of this research endeavor is dedicated to the meticulous analysis and extraction of zinc ions, a notorious constituent known for its high carcinogenicity, from wastewater compositions. By delving into the intricate complexities of isolating and quantifying this hazardous element, this study aims to shed light on the critical importance of mitigating the presence of zinc ions in wastewater to safeguard environmental integrity and public health.

2. Materials and Methods

The experimental data obtained from the analysis were meticulously documented employing a sophisticated setup comprising a graphite-based electrochemical sensor, a reference electrode saturated with potassium chloride, and an electrolyzer featuring an auxiliary graphite electrode with an expansive surface area. Furthermore, the research apparatus included the utilization of an ABC-1.1 device integrated with a computer system for data processing and analysis. Noteworthy instrumentation incorporated in the study encompassed an ACZET PVT LTD CY 224C analytical balance, a high-precision Swiss-made pH meter model pH/Mv/TEMP m FiveEasy F20, and a cutting-edge magnetic stirrer model MS-H280-Pro, each playing a pivotal role in ensuring the accuracy and reliability of the experimental procedures [3].

3. Results and Discussion

We started this research work by first preparing our working device and electrochemical sensor. For this:

1. Preparing the voltage analyzer for work.

The analyzer, the electrochemical sensor "EM-04 module" and the personal computer should not be installed on a table in a room with minimal vibrations from sources of strong electromagnetic fields (power transformers, electric motors, electric furnaces).

The "EM-04 module" is connected to the microprocessor unit via a cable to the corresponding connector on the back panel of the ABC - 1.1 voltammetric analyzer.

Connect the analyzer and the computer to the power source.

2. Preparation of electrodes for use.

   2.1. Preparation of EVL - 1M4 reference electrode.

Before use, the electrode should be prepared as follows:
- The rubber ring is moved down;
- The electrode cavity is washed with bidistilled water;
- Using a pipette from the filling hole, the electrode space is filled with a saturated solution of potassium chloride;
- The electrode is left in a saturated solution of potassium chloride for 48 hours;

   2.2. Preparation of the measuring (working) electrode.

Before using the working electrode (ES), the working surface of the measuring electrode must be wiped with ethyl alcohol and washed with bidistilled water, which prevents moisture from entering the threaded hole.

In our further work, we chose favorable conditions for zinc ion determination by inversion voltammetric (IV) ES method. First of all, the influence of the background electrolyte in the determination of zinc ion by the IV method was studied.

Control of the electrochemical reaction requires control of the role of the background electrolyte and buffer mixture in the proton-donating activity of the medium and the concentration of the detectable ion within strictly defined limits throughout the electrolysis. During the experiments, the following solutions are used as background electrolytes: 0,1 M H_3PO_4; 0,2 M HCl; 1,0 M KSCN; 0,1 M H_3PO_4 +0,1 M KNO_3; 1,0 M KCl + 0,2 M HNO_3; 1,0 M LiCl; 1,0 M KNO_3 va 1,0 M $NaNO_3$ + 1,0 M HF. We used different volumes and concentrations of these background electrolytes and buffer mixtures [4].

Before selecting the background electrolyte, zinc ion was determined in the presence of ordinary bidistilled water. First, we took 1.0 ml of the standard solution (10,000 $\mu g/dm^3$) containing zinc ions to be determined, put it in the electrochemical cell, and added 24 ml of bidistilled water. No analytical signal was observed when the resulting solution was analyzed. The reason is the low electrical conductivity of the solution, as well as the low activity of metal ions detected in the solution. In such cases, the use of background electrolyte solutions is appropriate and ensures the reliability of the analysis. The obtained results are presented in Figure 1.
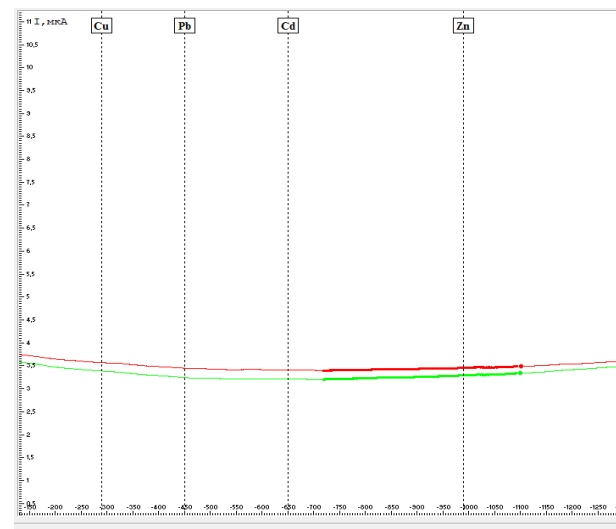
Figure 1. Graph of determination of zinc ion from standard solution without background electrolyte

It can be concluded from this picture that we will not be able to determine solutions containing zinc ions directly in the presence of bidistilled water. In such cases, it is necessary and appropriate to use background electrolytes and buffer mixtures [5].

Taking into account the above, 1.0 ml of the zinc standard solution was taken and different volumes and concentrations of background electrolytes and buffer mixtures were added. In this process, the formation of intensive zinc ion peaks was observed, and the volume and concentration of the appropriate background electrolyte were selected depending on the best analytical signal. The obtained results are presented in Figure 2 and Table 1.
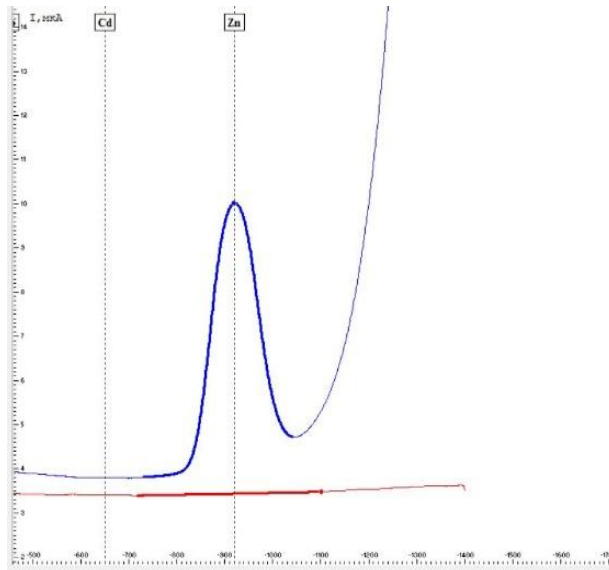
Figure 2. Effect of background electrolyte in the determination of zinc ion from a standard solution

Table 1. Effect of background electrolyte in inversion voltammetric determination of zinc ion (amperage=2,0 µA; t=120 s; C_{Zn} =10 µg/dm^3)

Background electrolyte nature and concentration	Zn^{2+}	
	E, mV	Hx, µA
0,1 M H_3PO_4	-900	8
0,2 M HCl	-920	18
0,1 M KSCN	-1100	11
0,1 M H_3PO_4+0,1 M KNO_3	-990	22
1,0 M KCl+0,2 M HNO_3	-930	17
1,0 M LiCl	-790	12
1,0 M KNO_3	-830	10
1,0 M $NaNO_3$ + 1,0 M HF	-880	13

As can be seen from the results in Table 1, the best results were observed when zinc was determined in the background electrolyte of 0.1 M H_3PO_4 + 0.1 M KNO_3. Therefore, all subsequent studies were carried out in accordance with the established optimal concentrations of this background electrolyte.

In our further studies, the influence of the amount of current and the collection time on the determination of zinc ion using the inversion voltammetry method was studied.

It is known [6,7] that one of the main factors that significantly affects the results of the analysis in the organization and conduct of the analysis process is the time of the analysis. Taking this into account, we have studied in our research that the time of accumulation of metal ions on the surface of ES has a significant effect on the height of the anode and cathode peaks and on the detection results.

The effectiveness of using the first two properties generally depends on the design of the commonly used device, while the effect of the depolarizer collection time on the AS value depends on the nature and concentration of the detected ions. The direct (linear) relationship between the quantity of the substance being determined on the electrode

and the duration of electrolysis in inversion analysis is important and of particular importance. In the calibration graph (KG) and addition method (QQ), the necessary criteria are the duration of the depolarizer accumulation on the working electrode and the dissolution of the electroactive substance in the analyzed solution, as well as the electrolysis processes, which must be the same in all measurements [10].

The results of the studies are presented in table 2 and figure 3, where the relationship between the time of zinc ions accumulation on the surface of the graphite-based working electrode and the height of the analytical signal is presented.

Table 2. The analytical signal dependence table of zinc ion accumulation time on the working electrode surface Zn^{2+} background – 0,1 M H_3PO_4+0,1 M KNO_3; amperage=2,0 µA; E = - 0,99 V; C_{Zn} = 1,0 µg/ml

Peak height, H, µA	1,3	3,3	5,7	8,2	9,6	11,2	12,3	13,8
Meeting time t, s	30	50	70	90	110	120	200	300
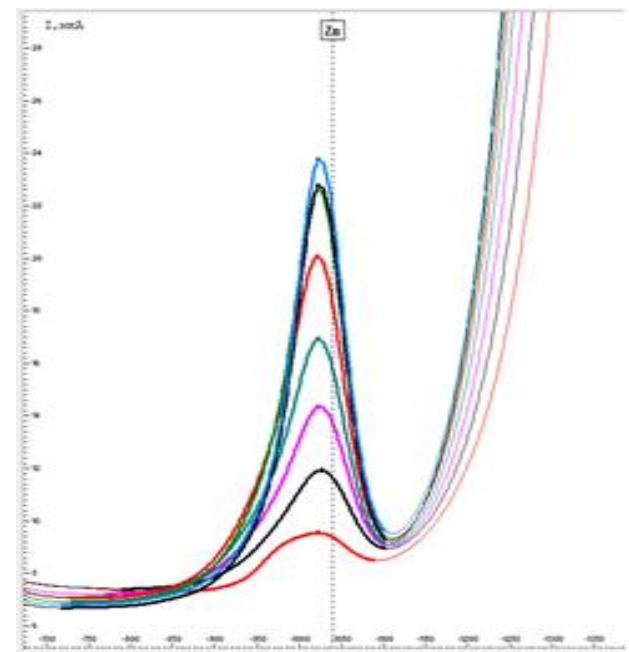
Figure 3. Graph of the dependence of the analytical signal on the concentration of zinc ions in the determination of zinc ions by the inversion voltammetric method

As can be seen from table 2 and figure 3, the optimal time for the accumulation of zinc ions on the surface of the working electrode is 120 seconds, because with the further increase of the electrolysis time, the peak heights become functions of their accumulation and reach constant values. and therefore it is not advisable to increase it further.

Choosing the best optimal conditions for the determination of zinc using the inversion voltammetry method and the accuracy and reliability of the obtained experimental data cannot be said without determining the zinc ion at different concentrations. In order to assess the accuracy of the developed methods for the detection of the studied metal, the following results are shown with parallel comparisons.
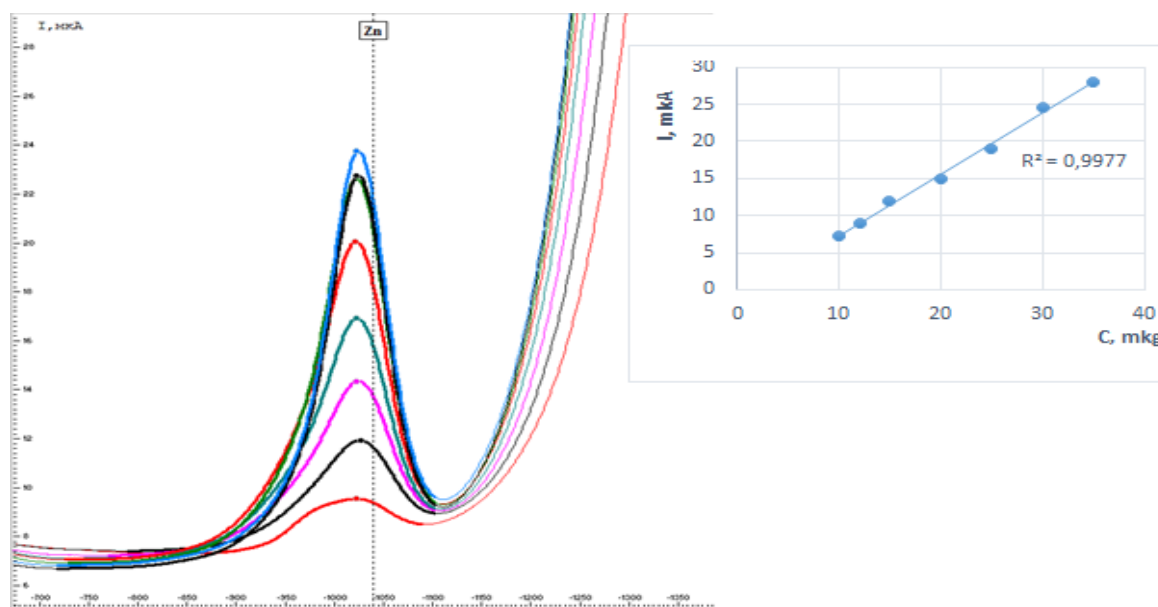
Figure 4. Graph of the dependence of the analytical signal on the concentration of zinc ions in the determination of zinc ions by the inversion-voltammetric method

Table 3. Zinc ion by inversion voltammetric method results of determination in individual solutions in different amounts

The nature of the ion and its background	Entered Zn^{2+}, μg	Found Zn^{2+}, μg	n	S	S_r
Zn^{2+} Background electrolyte: 0,1 M H_3PO_4+0,1 M KNO_3	1,0	1,09 ± 0,11	5	0,09	0,083
	2,0	1,96 ± 0,14	5	0,11	0,056
	4,0	4,08 ± 0,25	4	0,16	0,040
	8,0	7,90 ± 0,29	4	0,18	0,037
	16,0	16,81±0,23	5	0,21	0,031
	32,0	31,92±0,26	5	0,24	0,038

From the given results, it can be concluded that good results were achieved in the determination of zinc from separate solutions using the developed inversion voltammetric method, because in all cases it was observed that the relative standard deviation (Sr) did not exceed 0.083, which indicates the absence of systematic errors.

It can be seen from the results that the accuracy of the method of inversion-voltammetric determination of zinc ions is high and the correlation coefficient is equal to 0.9977 in the determination of zinc.

The correctness of the obtained data is concluded by the complete matching of the heights of the studied cations (in the analysis and standard solution), and the exact amount of the detected metal is calculated by the increase of AS due to additives. After determining the exact concentrations of zinc and its individual solutions, the analysis of model mixtures is carried out [9].

Binary, ternary and complex artificial mixtures were prepared according to the concentrations and compositions of real objects, according to which these metals and foreign cations and destructive anions occur together with them in nature.

Some of the data we obtained from the analysis of model mixtures for zinc determination are presented in Table 4 below.

After studying the possibility of detecting zinc from indium solutions using the method proposed by us, we should consider the effect of adjacent cations in the detection of zinc ions in natural objects. In order to check the possibility of increasing the detection level of the method by adding cations that are often found together in the composition of natural objects to the analyzed solution in the detection of zinc ion using the inversion voltammetry method, one of the interfering cations in the ratio of evaluating the selectivity and selectivity of these methods is used. Many experiments have been carried out in the presence of ionizing cations for the IV determination of zinc with the participation of several species [8]. The results of some experiments obtained by us are presented in Table 5, in which the results of the influence of adjacent cations on the accuracy and selectivity of the determination of 20 μg of zinc in 25 ml of the analyzed solution by the IV method are presented.

From the results of determination of zinc in the presence of cations related to zinc, it can be seen that foreign related cations do not interfere with the determination of the studied metals up to limited concentrations. The half-wave potential of the detected metal is of great importance in reducing the effect of neighboring cations. We increased the half-wave potential difference of zinc and its neighboring cations by properly choosing the background electrolyte.

The data obtained from the analysis served as the basis for the possibility of zinc determination in the presence of foreign cations in the nature and concentration of these metals, in turn, do not interfere with the determination of zinc, and when encountered together with the zinc ion in various objects. as long as it is possible.

Table 4. Effect of covalent cations on inversion voltammetric determination of zinc ion background – 0,1 M H_3PO_4+0,1 M KNO_3; amperage=2,0 μA; E = - 0,99 V; C_{Zn} = 1,0 μg/ml

[Zn]:[X]	Found Zn, μg	n	S	S_r
Zn:Cu 1:100	0,99±0,08	5	0,074	0,071
Zn:Cd 1:1	0,93±0,37	5	0,323	0,348
Zn:Pb 1:80	0,99±0,14	4	0,125	0,126
Zn:Cr 1:10 1:50	0,99±0,095 0,95±0,10	5 5	0,08 0,084	0,083 0,089
Zn:Mn 1:100	0,96±0,10	5	0,09	0,094
Zn:Sb 1:0,5	0,87±0,39	4	0,342	0,393

Table 5. Results of inversion-voltammetric detection of zinc ion from complex model mixtures (amperage=2,0 μA; t=120 s. R=0.95)

Composition of the analyzed mixture, μg	Found Zn^{2+}, μg (P=0,95; n=5)		
	$\bar{x} \pm \Delta X$	S	S_r
Zn(1,0)+Cr(2,0)+Cu(1,0)	1,04±0,13	0,11	0,105
Zn(1,0)+Cr(2,0)+Cd(0.1)	0,981±0,084	0,07	0,075
Zn(2,0)+Cr(1,0)+Pb(15)	1,99±0,10	0,09	0,045
Zn(1,0)+Cr(1,0)+Cd(0,3) +Cu(10,0)	0,971±0,122	0,11	0,109
Zn(3,0)+Cr(5,0)+Fe(15,0) +Mn(10,0)	2,90±0,29	0,25	0,086
Zn(0,5)+Cr(3,0)+Cd(0,5) +Cu(10,0)+Fe(30,0)	0,509±0,072	0,06	0,123

As can be seen from the results in this table, it is possible to determine IVA of zinc in real natural objects, in particular in complex model mixtures based on soil composition, where the value of Sr does not exceed 0,123 in all cases, which in turn indicates the accuracy and efficiency of the developed method. will give.

4. Conclusions

In the determination of zinc ion by inversion voltammetric method, favorable conditions were selected (pH value of inversion buffer mixture as background electrolyte is 5.6, and 0,1 M H_3PO_4+0,1 M KNO_3, accumulation time on the electrode surface is 120 seconds).

Using the developed method, zinc ion was determined from individual, binary and model artificial mixtures. The obtained results showed that it is possible to determine zinc ion from individual, binary and model artificial mixtures with the help of our developed method, and the relative standard deviation did not exceed 0.083.

Using the created inversion voltammetric method in the analysis of model binary, ternary and complex mixtures, it was possible to draw a conclusion from the results obtained in the inversion voltammetric determination of the studied metal, according to which the developed methods are similar in nature and concentration to real natural objects and showed that it can be used in soil.

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