DEVELOPMENT OF AN INVERSION VOLTAMMETRIC METHOD FOR DETERMINING Pb^{2+} IONS IN WASTEWATER

Ravshanova Munira
Termez State University Master's student
ravshanova985@gmail.com

Abstract. This article analyzes the theoretical and practical foundations for developing an inversion voltammetric method to determine Pb^{2+} ions in wastewater. The relevance of the topic is обусловлена? Need avoid Russian. Rewrite. The relevance of the topic is determined by the high toxicity of lead, its persistence in aquatic environments, and its ability to pose biological hazards even at low concentrations. The text examines, as an integrated system, the physicochemical essence of inversion voltammetry, its preconcentration stage and anodic recording process, as well as such factors as electrode material, supporting electrolyte, potential regime, time parameters, and matrix effects. Based on the work of Uzbek scientists, bismuth-modified carbon electrodes and biosorption-based preconcentration approaches are substantiated as among the most suitable directions specifically for Pb^{2+} monitoring. Local studies have shown a working range of 10–160 μg/dm³ and $R^2 \geq 0.98$ for the determination of Pb^{2+} and Cd^{2+} on Bi-modified electrodes, while some industrial laboratories have achieved detection down to 10 μg/L with a relative error of about 5%. On this basis, a methodological solution is proposed that relies on sample preparation for wastewater, electrode selection, optimization of the working medium, calibration by the standard addition method, and verification of results under complex matrix conditions.

Keywords. Pb^{2+}, wastewater, inversion voltammetry, anodic stripping voltammetry, bismuth-modified electrode, supporting electrolyte, biosorption preconcentration, standard addition method, electrochemical monitoring.

Introduction.

Lead is one of the most hazardous metal pollutants from ecological and sanitary perspectives. The World Health Organization notes that lead exposure damages many systems of the human body, and that the risk is especially high for children and women of reproductive age. According to WHO data, more than 1.5 million deaths in 2021 were associated with lead exposure, and there is no exposure level that can be considered safe. The presence of lead in aquatic environments is particularly important because it can enter drinking water, irrigation chains, or recycled process water. WHO maintains 10 μg/L as a provisional guideline value for drinking water and recommends keeping concentrations as low as possible. Under such conditions, a rapid, sensitive, and economical method for determining Pb^{2+} in wastewater is not merely a laboratory issue, but an instrument of environmental safety.

In the Uzbek scientific school, a distinct research tradition has developed in analytical chemistry, chemical sensors, and modified electrodes, associated with such researchers as Academician Sh.T. Tolipov, A.M. Gevorgyan, M.A. Nasimov, and Z.A. Smanova. Local authors have developed practical solutions for determining heavy metal ions using carbon-paste, carbon-graphite, and bismuth-modified electrodes. The strength of this school lies in the fact that the studies did not remain at a purely theoretical level, but were linked to real objects such as zinc electrolytes, wastewater, natural waters, and process solutions. In developing a method for determining Pb^{2+} ions in wastewater, it is precisely this local experience that should serve as the foundation, because the value of a method lies not only in maximum sensitivity, but also in its reproducibility under domestic laboratory conditions, low cost, and adaptability to industrial monitoring.

Literature Review.

An analysis of the work of Uzbek researchers shows that inversion voltammetry was not chosen in this field by chance. In N.A. Atakulova's dissertation abstract, the development of a detection method using modified electrodes was structured as a consistent scientific task that included selecting the modifier, determining optimal conditions, identifying the half-wave potential, evaluating analytical and metrological characteristics, testing interfering ions, and applying the method to real samples. This approach is directly applicable to the determination of Pb^{2+} in wastewater, because the main problem is not simply detecting the presence of the ion, but reliably isolating and quantifying it in a complex ionic and organic matrix. Local literature shows that modified carbon-paste electrodes can improve sensitivity, selectivity, and the working concentration range.

One of the most important local results directly relevant to Pb^{2+} is the work of S.D. Aronbayev and co-authors on bismuth-modified carbon electrodes. In that study, bismuth was shown to be a suitable modifier for stripping analysis because it is far less toxic than mercury and is capable of forming intermetallic systems with many heavy metal ions. The authors demonstrated the possibility of determining trace amounts of Pb^{2+} and Cd^{2+} using Bi-modified electrodes, and reported a working range of 10–160 $\mu g/dm^3$ for Pb^{2+} with a calibration curve showing R^2 of at least 0.98. The experimental conditions were also clearly specified: $0.2\ M\ HCl + 0.5 \cdot 10^{-4}\ M\ Bi(NO_3)_3$, $pH < 1$, $E_{acc} = -1.2\ V$, $t_{acc} = 60\ s$, and a scan rate of 50 mV/s. These data provide a ready-made local foundation for developing a Pb^{2+} method.

A second important direction in local sources is associated with preconcentration. In Aronbayev's doctoral research, a method was developed for the inversion voltammetric determination of Cd^{2+}, Pb^{2+}, and Cu^{2+} in aqueous media using biosorbents based on yeast cell walls. It was shown that this approach can increase sensitivity by one to two orders of magnitude and keep the error below 10%. In addition, Pb^{2+} exhibited a higher tendency toward biosorption than Cd^{2+} and Cu^{2+}, and a flow rate of 2–5 mL/min was found optimal for effective sorption under dynamic conditions. This result is highly important for wastewater analysis, because in real samples Pb^{2+} is often detected more accurately after preconcentration due to the presence of background ions and organic matter.

Analysis and Results.

The essence of inversion voltammetry in the determination of Pb^{2+} is based on a two-stage process. First, at a certain potential, the ions are accumulated on the electrode surface or reduced to the metallic state and preconcentrated. Then, when the potential is shifted in the anodic direction, the accumulated substance passes back into solution, and the resulting current maximum is proportional to the amount of analyte. The main advantage of the method is that the analytical signal is amplified by the mass accumulated during the preconcentration stage. For this reason, for trace metal ions such as lead, this approach can work at low concentrations even without expensive instruments such as atomic absorption spectrometers or ICP systems. The practical value of stripping voltammetry is also confirmed by the fact that the U.S. EPA has described a method for determining lead in water by differential pulse anodic stripping voltammetry as an official method.

The most important stage in the development of a methodology for determining Pb^{2+} in wastewater is sample preparation. If the aim is to determine dissolved Pb^{2+}, the water sample should be passed through a 0.45 µm filter in the field or immediately upon arrival at the laboratory, and the filtrate should be acidified with HNO_3 to $pH < 2$. If the aim is to determine total recoverable lead, the sample should not be filtered, but instead acidified directly and homogenized before analysis. This exact approach is recommended in EPA Method 200.8. Because wastewater contains a large amount of suspended matter, colloids, and organic substances, neglecting this stage may lead to shifts in voltammetric peaks or underestimation of the signal. Therefore, more than the "physical sensitivity" of the method, it is "sample discipline" that becomes the decisive factor.

Based on local results, the main recommended working scheme for Pb^{2+} can be formulated as follows. A three-electrode cell is used. The working electrode is an ex situ bismuth-modified carbon-graphite paste electrode, the reference electrode is

Ag/AgCl, and the auxiliary electrode is made of an inert material. The supporting electrolyte is selected as 0.2 M HCl + $0.5\cdot10^{-4}$ M $Bi(NO_3)_3$. The accumulation potential is –1.2 V, the accumulation time is 60 s, the potential sweep range is from –1.2 to +0.3 V, the alternating voltage amplitude is 20 mV, and the scan rate is 50 mV/s. In local studies, linearity for Pb^{2+} was observed under exactly these conditions in the 10–160 μg/dm³ range. This interval can be considered a practically sufficient starting zone for many wastewater monitoring situations.

In such a methodology, calibration is more appropriately performed not by an external standard method, but by the standard addition method. The reason is that the ionic strength of wastewater, chloride content, surfactants, dissolved organics, and multimetal character do not affect the electrode process uniformly. In local doctoral research, the “method of additions” and the “introduced–found” approach were used as reliability criteria for real, model, and reference samples. Applying the same approach to Pb^{2+} protects the analytical result from matrix-related errors. In practice, this means that known concentrations of a Pb^{2+} standard solution are added to three or four aliquots of the same sample, and the initial amount is recalculated from the change in peak height. This method appears simple, but for complex objects such as wastewater it is one of the most correct approaches.

If the Pb^{2+} content in the sample is very low or the matrix is highly aggressive, it is advisable to introduce a biosorption preconcentration stage into the method. Aronbayev’s work demonstrated that Pb^{2+}, Cd^{2+}, and Cu^{2+} can first be accumulated on a biosorbent based on yeast cell walls, then desorbed, and finally determined by inversion voltammetry. According to the authors’ data, this approach increased sensitivity by one to two orders of magnitude, kept the error below 10%, and was implemented in the practice of the Navoi Mining and Metallurgical Combine. Another local source reported that, using a bismuth electrode, Cd^{2+} and Pb^{2+} could be determined in wastewater and natural waters down to 10 μg/L, with a relative error of about 5%, and that the method was introduced into the laboratory of the Muborak Gas Processing Plant. These results make it possible to evaluate the proposed methodology for wastewater not as a theoretical concept, but as a practical solution.

The issue of electrode material is of particular importance in the determination of Pb^{2+}. Historically, mercury electrodes have been highly sensitive in stripping analysis, but their high toxicity creates serious limitations from both ecological and laboratory safety perspectives. Local authors therefore selected bismuth as a suitable alternative. Bismuth is also capable of forming intermetallic phases, but its toxicity is significantly lower than that of mercury. In addition, Aronbayev and co-authors showed that, in a solution containing a Bi-modified electrode, the Cu^{2+} peak is not expressed as strongly as it is on classical mercury electrodes. This may reduce the influence of certain neighboring cations during Pb^{2+} determination. In the work of N.A. Atakulova, D.A. Ziyayev, and co-authors on copper and zinc, it was also shown that modified graphite electrodes allow the inversion voltammetric determination of several metal ions in one sample. Thus, the method being developed for Pb^{2+} can in the future be expanded into a multielement monitoring format.

Based on local literature, the analytical characteristics of the proposed method for determining Pb^{2+} in wastewater can be summarized as follows. When working directly with a Bi-modified electrode, the linear working range is formed around 10–160 µg/dm³. If biosorption preconcentration is used, the sensitivity increases by one to two orders of magnitude, and the method can reach down to about 10 µg/L. In local voltammetric studies, a control level of 0.06 mg/dm³ for Pb^{2+} in wastewater monitoring has been mentioned. This means that the proposed method is sufficient not only for controlling that level, but also for working at values below it. In this respect, the method is suitable not merely for “presence or absence” testing, but also for evaluating wastewater treatment efficiency and controlling recycled water systems.

Discussion.

The advantage of inversion voltammetry for determining Pb^{2+} in wastewater lies in its simplicity, its suitability for automation, low reagent consumption, increased sensitivity through pre-accumulation of the analyte on the electrode surface, and the possibility of use near the object of study. Local review papers note that precisely these characteristics make electrochemical control methods preferable for environmental objects. Recent local work on screen-printed and modified carbon electrodes shows a movement toward miniaturization, disposable sensors, and monitoring tools adapted to field conditions. This creates the possibility of moving Pb^{2+} monitoring beyond large centralized laboratories.

The weaknesses of the method are also clear. Wastewater is not ordinary water. It contains dissolved salts, suspensions, organic matter, multivalent cations, complex-forming anions, and sometimes technological additives occurring together. Local dissertation studies have also shown that the identification of interfering ions, testing of model mixtures, selection of the optimal supporting electrolyte, and separate assessment of metrological properties are mandatory parts of the research. Here, the main error often lies not in electrode material selection, but in insufficient evaluation of matrix effects. In an ideal solution, the relationship between the actual concentration of Pb^{2+} and the peak on the voltammogram is simple, but in real wastewater it becomes reliable only with an adapted methodology. For this reason, sample preparation, the standard addition method, repeated measurements, blank control, and, when necessary, preconcentration must be treated as integral components of the method.

Among the directions for further development, three appear especially strong. The first is the introduction of mercury-free, environmentally safe electrodes. In this regard, bismuth electrodes have justified themselves in local practice. The second is the integration of biosorption preconcentration into the methodology. This makes it possible to capture Pb^{2+} even at very low levels and combines wastewater treatment technology with analytical control into a single chain. The third is the development of miniaturized solutions such as screen-printed electrodes, ergonomic sensors, and “drop-based measurement” formats. Local studies report that a patent has been obtained for an electrochemical sensor, that there are developments involving Bi-modified screen-printed electrodes, and that this direction is expanding. This indicates that creating an inexpensive and portable technological platform for Pb^{2+} monitoring under Uzbek conditions is a realistic task.

Conclusion.

In developing an inversion voltammetric method for determining Pb^{2+} ions in wastewater, two directions of the local school of analytical chemistry are of particular importance as foundational points. The first is the use of bismuth-modified carbon electrodes, and the second is biosorption-based preconcentration. Bismuth electrodes provide the sensitivity required for lead determination, relatively low toxicity, and the possibility of application to real water objects. The biosorption stage reveals the true capacity of the method when working with low concentrations, complex matrices, and industrial wastewater. On this basis, standardizing sample preparation for Pb^{2+}, using a supporting system based on 0.2 M HCl + Bi(III), employing a preconcentration regime at –1.2 V, calculating results by the standard addition method, and introducing biosorption preconcentration where necessary appear to be the most substantiated methodological solution for laboratories in Uzbekistan. Such an approach can bring environmental monitoring to a reliable level even without expensive instrumental complexes.

References

1. Aronbaev S.D., Aronbaev D.M., Narmaeva G.Z. Carbon-containing environmentally friendly electrodes modified with bismuth for voltammetric analysis. Universum: Chemistry and Biology. 2018. No. 5(47). URL: electronic resource.

2. Aronbaev S.D. Sorption concentration and determination of ecotoxicants using biosorbents based on the cell walls of brewer’s yeast: abstract of dissertation for the degree of Doctor of Chemical Sciences. Tashkent, 2016.

3. Atakulova N.A. Improvement of the method for the determination and separation of selenium and tellurium ions in zinc electrolyte: dissertation abstract for the degree of Doctor of Philosophy in Chemistry. Tashkent, 2022.
4. Atakulova N.A., Ziyayev D.A., Sayfiev M.N., Bokiev K.S. Optimization of inversion voltammetric determination regimes for copper and zinc on graphite-containing modified electrodes. Andijon Ilmiy Xabarnomasi. 2022. No. 5. pp. 26–30.
5. Sayfiev M.N., Bokiev Q.S., Ziyayev D.A. Determination of Copper(II) Ion Together with Cadmium from Wastewater by Inversion-Voltamperometric Method. Proceedings of International Conference on Modern Science and Scientific Studies. 2024. Vol. 3, No. 1. pp. 129–132.
6. Aronbaev S.D., Narmaeva G.Z., Aronbaev D.M. Inversion voltammetric determination of lead and cadmium using Bi-modified electrodes. In: Abstracts of the Republican Scientific and Technical Conference “Modern Problems and Prospects of Chemistry and Chemical-Metallurgical Production”. Navoi, 2018. pp. 213–215.
7. Narmaeva G.Z., Isakova D.T., Aronbaev S.D., Aronbaev D.M., Ismailov E.Kh. Inversion voltammetric determination of Cd(II) and Pb(II) in wastewater and natural waters using Bi-modified electrodes. In: Abstracts of the International Symposium “Central Asia 2020 (GSI-VIII)”. Nur-Sultan, 2020. pp. 51–55.
8. Ismailov E.Kh., Aronbaev D.M., Narmaeva G.Z., Isakova D.T., Aronbaev S.D. Inversion voltammetric determination of Cd(II) and Pb(II) in wastewater and natural waters using screen-printed electrodes modified with bismuth. In: Proceedings of the 3rd All-Russian Conference “Methods for Studying the Composition and Structure of Functional Materials”. Novosibirsk, 2020. pp. 403–404.
9. Aronbaev S.D. et al. Screen-printed electrodes in inversion voltammetric determination of heavy metals. Universum: Chemistry and Biology. 2020. No. 5(71). URL: electronic resource.