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Research Article

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The application of screen-printed electrodes and bath – injection cells for real-time and in-site voltammetric analysis of heavy metals

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Abstract: This study aims to develop and experimentally implement a novel portable electrochemical sensor based on screen-printed carbon electrodes (SPCEs) and an original bath-injection electrochemical cell for real-time environmental monitoring of pollutants. The scientific novelty of this work lies in the design of a simplified yet highly effective electrochemical cell that eliminates the need for a liquid carrier through an innovative self-washing mechanism using excess sample volume. This feature significantly reduces system complexity and enhances sensor reliability in field applications. The advantages of microfluidic technologies in the development of SPCE-based sensors are highlighted, and detailed protocols for modifying SPCEs with mercury, bismuth, and gold films are presented. Surface characterization is supported by micrographs, ensuring reproducibility of the electrode surface and analytical results. Voltammograms for various individual ions and their mixtures are provided, along with the corresponding electrode modifications and analytical conditions. The developed system demonstrates a broad linear concentration range and a detection limit as low as 5–10 μg/L. Field trials of the sensor were conducted using water samples from the Zeravshan river, a major source of drinking water in the region. Elevated concentrations of several toxic ions were detected, with the results confirmed by atomic absorption and inductively coupled plasma atomic emission spectroscopy. The proposed sensor system proves to be a promising solution for on-site pollutant detection under limited infrastructure conditions, supporting rapid response to both anthropogenic and natural environmental emergencies.

Keywords: screen-printed electrodes; stripping voltammetry; electrochemical micro-cell; bath-injection systems; on-site and real-time pollution analysis

1 Introduction

One of the key priorities in modern analytical chemistry is the creation of reliable, real-time methods for on-site chemical analysis [1–3]. The demand for such approaches has grown significantly due to their critical role in rapid decision-making during man-made and natural emergencies, where analytical delays can lead to severe consequences [4–7]. In addition to emergency response, on-site analysis ensures the integrity of samples by minimizing alterations caused by environmental influences such as temperature shifts, UV exposure, redox activity, and time-dependent degradation processes like hydrolysis and aging.

The emergence of portable, compact, and automated analytical systems – especially those based on microfluidic

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technologies – has opened new avenues for decentralizing laboratory diagnostics [8–10]. Among these, “lab-on-a-chip” platforms incorporating screen-printed electrodes (SPEs) stand out for their high potential in miniaturized voltammetric analysis [11, 12]. These systems not only require minimal reagent and sample volumes but also offer high analytical performance, reproducibility, and ease of automation at low cost, making them especially attractive for field use and routine analysis in resource-limited settings [13–16].

Screen-printing technology enables the mass production of disposable electrochemical sensors with customizable design and functionality [17–19]. By tailoring the composition and rheology of carbon-based inks, it is possible to fabricate SPEs with diverse structural and electrochemical characteristics [20–23]. This includes the ability to modify electrode surfaces with various nanocomposite materials – such as metal or organic films – thus significantly expanding their selectivity and sensitivity [24, 25]. For example, carbon microparticles incorporated into the ink can enhance the sensor’s performance, enabling it to detect a broad range of analytes [26–29].

The use of SPCEs has been further advanced by the development of three-electrode sensor designs with standard dimensions of 10 × 28 × 0.35 mm, where carbon-based inks form the working and auxiliary electrodes, and silver chloride paste serves as the reference electrode [30, 31]. Additionally, dielectric substrates such as polyethylene terephthalate (PETF) or thick Whatman-type paper are commonly employed to support these sensors [32, 33]. These innovations have paved the way for more efficient and scalable production of high-performance electrochemical sensors.

Despite significant advances in planar voltammetric systems, most analytical measurements employing screen-printed carbon electrodes (SPCEs) are still conducted under static conditions [34–36]. For practical on-site applications and integration into continuous monitoring systems, however, the transition to a flow-through configuration is essential.

Flow injection analysis (FIA) offers several advantages: it eliminates the need for sample mixing or pretreatment, reduces reagent consumption, and enables automation [6, 37]. Nevertheless, the implementation of FIA requires the incorporation of additional mechanical components into the analytical platform – such as a peristaltic or plunger pump, a carrier flow-rate controller, and a sample injection device [38]. Furthermore, commercially available FIA systems are not always compatible with standardized SPCE sensors, which limits their widespread adoption, particularly for field applications.

In recent years, batch-injection analysis (BIA) has emerged as a practical alternative to FIA [39, 40]. BIA systems retain the main advantages of FIA – high sampling frequency, low sample and reagent consumption, good accuracy, sensitivity, and reproducibility – while avoiding the need for auxiliary components typically required in FIA setups (pumps, injectors, and carrier flow control systems) [41, 42].

Traditionally, all reported BIA cells have utilized three separate electrodes (working, auxiliary, and reference) [43–46], which can be cumbersome, especially when a conventional reference electrode is employed, as it requires special maintenance. The introduction of SPCE technology has largely resolved this issue since SPCEs inherently integrate all three electrodes on a single planar substrate.

Nevertheless, researchers continue to propose improved electrochemical cell configurations and simplified sample introduction systems [47–49], aiming to enhance portability, reduce manufacturing costs, and maintain analytical performance.

In this work, we propose a simple and cost-effective batch-injection analysis system based on both native and modified SPCEs. The primary objective is to assess its analytical characteristics and evaluate the feasibility of using such a system for real-time, on-site voltammetric determination of target analytes. The study underscores both the scientific and practical significance of integrating SPCEs into compact, portable BIA configurations, thereby advancing the development of rapid environmental and industrial electrochemical diagnostics.

2 Materials and methods

In this study, unmodified screen-printed electrodes (SPCEs) from RUSENS Ltd (Russia) were used as the base electrodes [31]. The modification of the working surface of these electrodes was performed using mercury, bismuth, and gold, employing both *in situ* and ex situ methods. These modifications were adapted from techniques traditionally applied to macroelectrodes, but with optimizations tailored to the SPCEs, making them more suitable for sensitive and selective measurements.

All reagents used in the work were qualified as “suitable for analysis” and “chemically pure” and were purchased from the main suppliers of reagents from Russia (CJSC

Reagent) Kazakhstan (Sigma-Aldrich), China (ALFA GROUP). Control solutions were prepared in bidistilled water with a specific electrical conductivity of no more than 0.5 µs/cm. The appropriate certified reference solution was used to prepare buffer solutions. The pH was monitored using a portable pH meter DPH1 (Fortek, Uzbekistan).

2.1 Surface modification methods

2.1.1 Mercury film modification

The modification of the SPCE surface with a mercury film was carried out using an *in situ* deposition process. A solution containing 5×10^{-4} mol·L^{-1} $Hg(NO_3)_2$ in 1 M sodium acetate buffer (pH 5.6) was employed. To ensure the removal of dissolved oxygen, the solution was purged with nitrogen for 10–15 min prior to the deposition. After deaeration, a potential of −1.0 V vs. Ag/AgCl was applied for 600 s to facilitate mercury film formation. Following this step, the electrode was thoroughly rinsed with distilled water to remove any residual solution.

2.1.2 Bismuth film modification

For the bismuth film deposition, the electrode was exposed to a solution containing 1 mg·L^{-1} Bi(III) in 0.1 M acetate buffer (pH 4.5) at −1.4 V (vs. Ag/AgCl) for 300 s. Prior to deposition, a conditioning step at +0.3 V for 5 min was performed to re-oxidize any heavy metals that might have been adsorbed on the electrode surface. During the deposition process, the solution was continuously stirred to ensure uniformity of the film. After modification, the electrode was rinsed with distilled water followed by ethanol to eliminate any residual chemicals.

2.1.3 Gold film modification

The gold film was deposited using a novel method outlined in RF patent RU2753352C1 [50], which involves the reduction of gold from its acidic form with sodium nitrite in a polyvinyl alcohol (PVA) solution.

$$2H[AuCl_4] + 3NaNO_2 + 8NaOH \rightarrow 2Au + 3NaNO_3 + 8NaCl + 5H_2O$$

A 100 mg·L^{-1} $H[AuCl_4]$ solution, prepared from certified reference materials provided in the TL-4 voltammetric analyzer kit (Tom-Analyte, Tomsk), was reacted with 10^{-3} M sodium nitrite in 1 % PVA solution. The reaction was initiated by the addition of 2M caustic soda, and the mixture was then sonicated at 40 °C for 20 min. The appearance of pink coloration in the solution indicated the formation of gold nanoparticles.

To modify the SPCE surface, a drop-casting method was employed, wherein the colloidal gold nanoparticle solution was applied to the working electrode surface and allowed to dry. To further stabilize the gold film, the electrode was subjected to cyclic voltammetry in 0.2 M hydrochloric acid, with a potential scan range of −0.2 V to −1.4 V vs. Ag/AgCl, repeated 15–20 times at a scan rate of 25–30 mV/s. This unique approach to gold nanoparticle deposition enhances the surface conductivity and electrochemical properties, enabling superior sensor performance.

2.2 Instrumentation

Electrochemical measurements were performed using a computerized PU-1 polarograph (Belarus), which digitized the analytical signal from the working electrode. This data was transmitted to a personal computer for analysis, where peaks corresponding to metal ions were identified and quantified. Cyclic voltammetry was conducted with an ELINS P-40X potentiostat/galvanostat, equipped with an FRA 24 module (Russia), for detailed electrochemical characterization. Additionally, atomic absorption spectroscopy and inductively coupled plasma atomic emission spectroscopy (ICP-AES) were employed using an ISP5000 spectrometer (Thermo Fisher Scientific, USA), providing complementary methods for metal ion quantification. The morphology of the modified electrode surfaces was examined using a Shimadzu SSX-550 scanning electron microscope (Japan), which provided high-resolution imaging of the films deposited on the SPCEs.

2.3 Research object

The study was carried out using model solutions containing various heavy metal ions, as well as real-world water samples collected from the city of Samarkand and the Zeravshan river. The heavy metal ion concentrations in these samples were quantified to evaluate the performance of the modified electrodes in environmental sensing applications.

Measurement accuracy was rigorously evaluated using standard statistical methods, including the *F*-test, to ensure reliable and reproducible results.

3 Results and discussion

The use of screen-printed electrodes (SPCEs) in electrochemical experiments enables rapid and convenient detection, enhances experimental efficiency, and contributes to the practicality and innovativeness of electrochemical sensing systems, thereby meeting market demands. Figure 1 shows the general configuration of a standard screen-printed electrode.

Early SPCEs used for the voltammetric determination of heavy metal ions – such as zinc, cadmium, lead, and copper – were modified in a manner similar to solid macroelectrodes, using mercury films formed both *in situ* and ex situ [51, 52]. Although mercury-modified SPCEs demonstrated low detection limits for heavy metals at micromolar and sometimes nanomolar concentrations, the use of mercury did not address the need for environmentally friendly electrodes.

As a result, researchers have focused on developing mercury-free and environmentally benign SPCEs, typically by modifying the surface with noble metal nanoparticles, metal oxides, various carbon nanostructures, and hexacyanoferrates [53–55]. Of particular interest is the bismuth-based electrode [56]. While its operational potential window is narrower than that of mercury, bismuth is nearly 5,000 times less toxic [57]. Additionally, bismuth and its salts are more readily available and environmentally safer. Like mercury, bismuth is capable of forming intermetallic compounds with many metals [58], and its film can be deposited onto electrode surfaces using techniques similar to those used for mercury, both *in situ* and ex situ, from solutions of bismuth salts [59].

These advantages have led to the growing use of bismuth as a surface modifier [60–63]. Since then, bismuth-modified electrodes have found applications in environmental monitoring [35, 64, 65], food analysis [66], pharmaceutical testing [67–69], and the analysis of biological fluids and plant materials [70]. Naturally, bismuth film modification has also been extended to screen-printed electrodes. However, information on Bi-SPCEs and their practical applications remains relatively scarce in the scientific literature. Therefore, a comprehensive study of the fabrication technology and practical use of bismuth-modified SPCEs remains a relevant and pressing issue.

In our study, we drew on prior experience in modifying macroelectrodes with bismuth films [71]. The bismuth-containing modifying solution was prepared by dissolving bismuth nitrate to a concentration of 1 mmol of Bi(III) ions in a 0.1 M sodium acetate buffer solution at pH 4.5. The Bi-SPCE

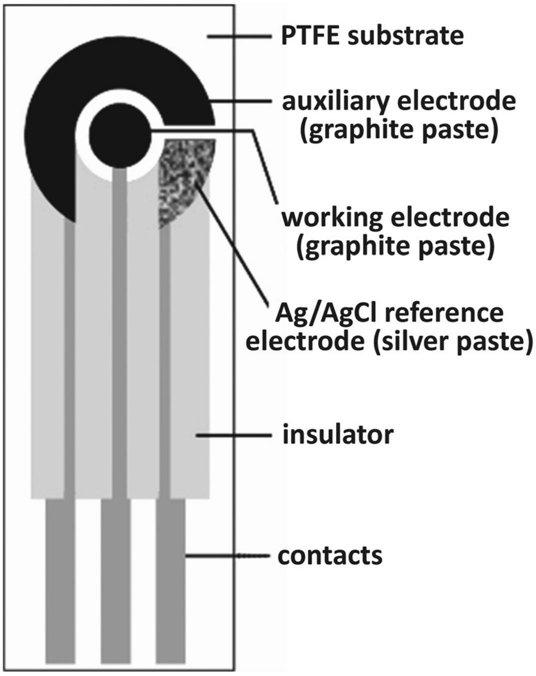

Figure 1: Scheme of screen printed electrodes.

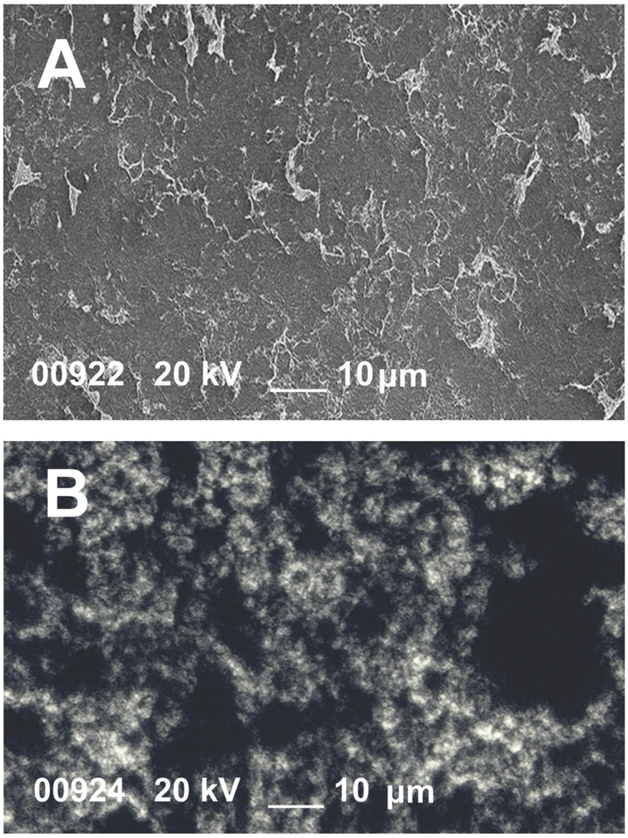

Figure 2: SEM images of unmodified (A) and bismuth-modified (B) screen printed electrodes.

was prepared as described in Section 2 (Materials and Methods). The success of the bismuth modification was confirmed by scanning electron microscopy (SEM).

Figure 2 shows SEM micrographs of unmodified (A) and bismuth film-modified (B) screen-printed electrodes. Comparative analysis of the micrographs revealed the appearance of contrasting regions and the formation of fibrillar structures in the Bi-SPCE image [72].

In a study [73], it was found that bismuth nanoparticles deposited on a graphitized substrate from the gas phase had an average radius of 56 ± 6 nm, whereas the particles formed during electrochemical deposition in our case had a radius of 150 ± 9 nm. Typically, the sizes of nanoparticles in the ash are smaller than those on the electrode surface. This phenomenon was explained by the possibility of bismuth nanoparticle aggregation during the drying of the gel deposited on the graphitized electrode base.

For voltammetry, a key factor confirming the successful modification of the indicator electrode is the acquisition of a reproducible voltammogram with clearly separated peaks corresponding to the metal ions present in the electrolyte.

Figure 3 presents the voltammogram of Cd^{2+} and Pb^{2+} in their combined presence, recorded on a Bi-modified SPCE electrode.

It was experimentally determined that the calibration plots for Cd^{2+} and Pb^{2+} exhibit linearity in the ranges of 10–120 µg/dm^3 and 10–160 µg/dm^3, respectively. These concentration dependences are shown in Figure 4.

The accuracy of the voltammetric determination of cadmium and lead ions in their joint presence was verified under laboratory conditions using the standard addition method, with recovery percentage calculations. The results are presented in Table 1.

The data in Table 1 confirm the potential of bismuth-modified electrodes for voltammetric analysis of real samples – specifically, for determining Cd^{2+} and Pb^{2+} ions in wastewater, surface water, and drinking water.

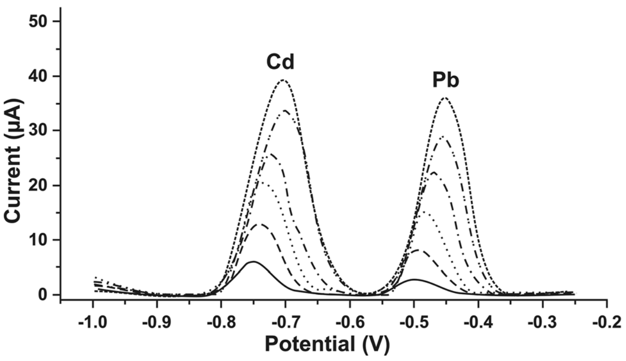

Figure 3: Voltammograms showing the dependence of the analytical signal on the increasing concentrations of Cd^{2+} and Pb^{2+} in model solutions, and the calibration graph *Conditions:* $E_{\text{appl}} = -1.4$ *V; accumulation time: 90 s; scan rate: 50 mV/s.*

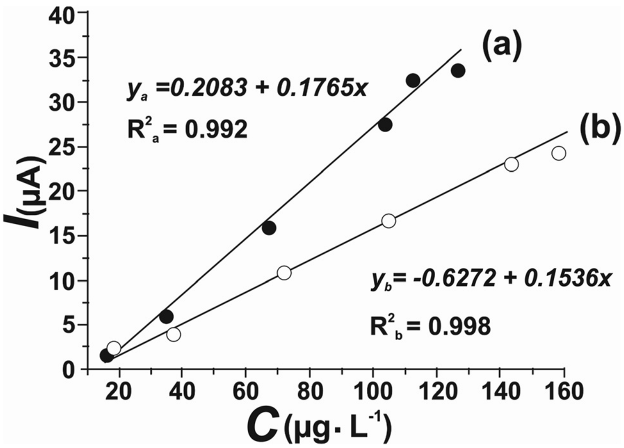

Figure 4: Calibration curves for the determination of Cd(II)(a) and Pb(II)(b) ions using Bi-SPCE.

Table 1: Results of the evaluation of the accuracy in determining Cd(II) and Pb(II) ion concentrations in model solutions by stripping voltammetry using Bi-SPCE.

Ion	Introduced, µg·L^{-1}	Found, µg·L^{-1}	R%
Cd(II)	5	4.60 ± 0.42	92.0
	10	9.76 ± 0.80	97.6
	20	18.8 ± 1.01	94.0
	50	47.3 ± 1.03	94.6
	100	101.6 ± 2.04	101.6
Pb(II)	10.0	10.2 ± 0.7	102.0
	20.0	18.2 ± 1.4	91.0
	40.0	38.1 ± 1.6	95.3
	80.0	84.8 ± 5.4	106.0

Table 2 shows selected results of Cd^{2+} and Pb^{2+} determination in these samples.

In this experiment, the results obtained by two independent methods – stripping voltammetry using a Bi-SPCE and atomic absorption spectroscopy (AAS) – were compared. Statistical evaluation of both datasets using Fisher's F-test and Student's t-test demonstrated that, for the given sample size (n = 5) and significance level (P = 0.95), the calculated values were significantly lower than the corresponding tabulated ones ($F_{\text{ex}} < F_{\text{tabl}}$ and $t_{\text{ex}} < t_{\text{tabl}}$). This indicates that there are no statistically significant differences between the results obtained by the two methods, and therefore, the analytical data can be combined.

Practical voltammetric analysis demonstrates that gold-based indicator electrodes, owing to their chemical inertness and high oxidation potential, offer a broader operational potential window and are thus more suitable for determining

Table 2: The results of the stripping voltammetry determination of Cd^{2+} and Pb^{2+} ions in aqueous media using the Bi-SPCE additive method ($n = 5$; $P = 0.95$; $F_{tabl.} = 6.4$; $t_{tabl.} = 2.31$).

Determined ion	Concentration of the introduced standard additions $\mu g \cdot L^{-1}$	Defined by stripping voltammetry with Bi- SPCE		Determined by AAS method		$F_{exp.}$	$t_{exp.}$
		Found, $\mu g \cdot L^{-1}$	S_r	Found, $\mu g \cdot L^{-1}$	S_r		
Industrial wastewater							
Cd^{2+}	–	6.80 ± 0.44	0.05	7.00 ± 0.25	0.04	1.6	0.4
	10	16.30 ± 0.68	0.04	17.10 ± 0.36	0.04		
	20	27.10 ± 0.82	0.04	27.50 ± 0.70	0.03		
Pb^{2+}	–	–	–	0.72 ± 0.06	0.04	2.2	0.56
	10	10.60 ± 0.07	0.01	11.23 ± 0.07	0.01		
	20	19.40 ± 0.06	0.01	20.20 ± 0.06	0.01		
The water from an artificial reservoir							
Cd^{2+}	–	–	–	1.60 ± 0.05	0.02	2.1	0.62
	10	11.02 ± 0.08	0.02	11.90 ± 0.07	0.03		
	20	21.22 ± 0.09	0.02	21.80 ± 0.07	0.03		
Pb^{2+}	–	18.47 ± 0.48	0.01	18.80 ± 0.32	0.01	2.6	0.32
	10	28.18 ± 0.41	0.03	29.10 ± 0.33	0.01		
	20	49.15 ± 0.70	0.01	51.20 ± 0.60	0.01		
Drinking water							
Cd^{2+}	–	–	–	0.52 ± 0.05	0.04	2.0	0.90
	10	10.72 ± 0.06	0.04	9.78 ± 0.07	0.05		
	20	20.56 ± 0.07	0.05	19.32 ± 0.05	0.05		
Pb^{2+}	0	9.19 ± 0.46	0.04	8.98 ± 0.28	0.03	2.4	0.69
	10	18.62 ± 0.28	0.01	19.12 ± 0.44	0.01		
	20	29.68 ± 0.60	0.02	28.92 ± 0.24	0.06		

various heavy metals. The modification of carbon-containing electrodes with gold typically involves electrolytic deposition from an $H[AuCl_4]$ solution, using either constant current (0.2–0.3 mA/cm^2) or constant potential (from −0.1 to +0.2 V). By varying the gold deposition time, one can form an irregular ensemble of gold microelectrodes with dimensions ranging from 100 to 1,000 nm on the surface.

Gold is readily reduced due to its high standard electrode potential (+1.498 V for the Au^{3+}/Au couple), making Au^{3+} cations strong oxidizing agents. This allows gold recovery from $HAuCl_4$ solutions using wet-chemical methods similar to those described in Section 2.

A micrograph of the SPCE surface modified with gold nanoparticles using the proposed method is shown in Figure 5.

Modified SPCEs were employed to determine individual metal ions in aqueous solutions under laboratory conditions using conventional stationary electrochemical cells with a total volume of up to 10 mL (Figure 6a). This approach enables the quantification of trace metal ions by the standard addition method; however, it requires continuous mixing of the solution, which limits its applicability in field conditions. Consequently, flow-injection techniques are often preferred. In these systems, the sample is introduced into a segmented liquid stream that is delivered to the electrochemical cell by means of a peristaltic pump or an alternative device (e.g., a pressurized vial). Examples of commercial electrochemical cells designed for SPCEs and operating in flow-injection mode are presented in Figure 6b and c. Nevertheless, the use of carrier-fluid delivery systems such as peristaltic pumps complicates the experimental setup and reduces its suitability for on-site applications.

In recent years, periodic injection systems have been proposed as a simplified alternative, allowing operation without continuous media flow. In such systems, a certain volume of the sample is injected directly onto the surface of the sensor using a syringe or an automatic pipette. The ΩMetrohm sensor shown in Figure 6d uses an electronic micropipette as a metering device, which increases both the complexity of the design and the cost of installation, since it additionally requires mechanical fixation and sealing of the pipette.

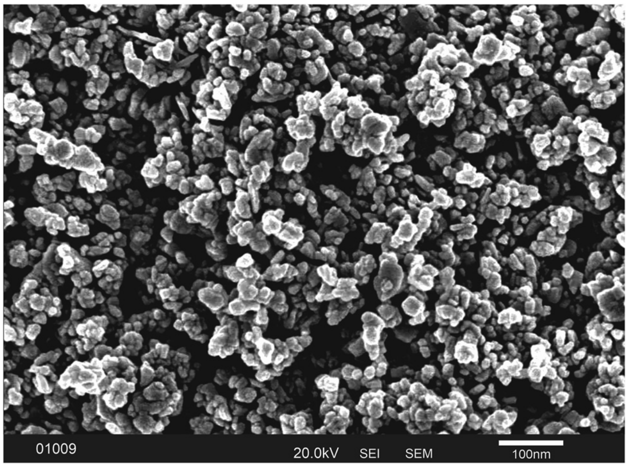

Figure 5: SEM image of the modified screen-printed electrode surface reveals the localization of gold micro- and nanoparticles, indicating successful electrode modification.

Detailed information about the design and manufacturing technology of the ΩMetrohm sensor has not been publicly disclosed. However, a comparative analysis of the cell we developed for periodic administration and the cell described in the literature [74] shows that the latter has a significant "dead volume" and does not have both a mechanism for removing the analyte after measurement and a built-in cell flushing system (Figure 7a).

For clarity, Figure 7 presents schematic diagrams of the compared electrochemical batch-injection cells. The cross-sectional view of our device (Figure 7b) clearly illustrates the principle of its construction and enables its independent fabrication.

The electrochemical sensor housing is made of transparent plexiglass and consists of an upper (1) and lower (2) part, fastened together with screws (3). A shaped slot (4) for a standard screen-printed electrode (5) is located between the housing parts, into which the electrode is inserted. The electrode is held in place by a threaded sleeve (6) screwed into the lower part. The upper part contains a sleeve (7) with a capillary (8) for introducing the analyte directly above the electrode surface. The SPCE sensor is connected to the measurement device.

Considering that only 15–20 µL of the analyzed solution is sufficient to completely cover the SPCE surface, the introduction of 500–1,000 µL of analyte into the cell ensures multiple rinsing of the electrode area (approximately 30–50 times). The cell is filled directly with the sample, while any excess solution is removed through a drainage tube. Such a design of the

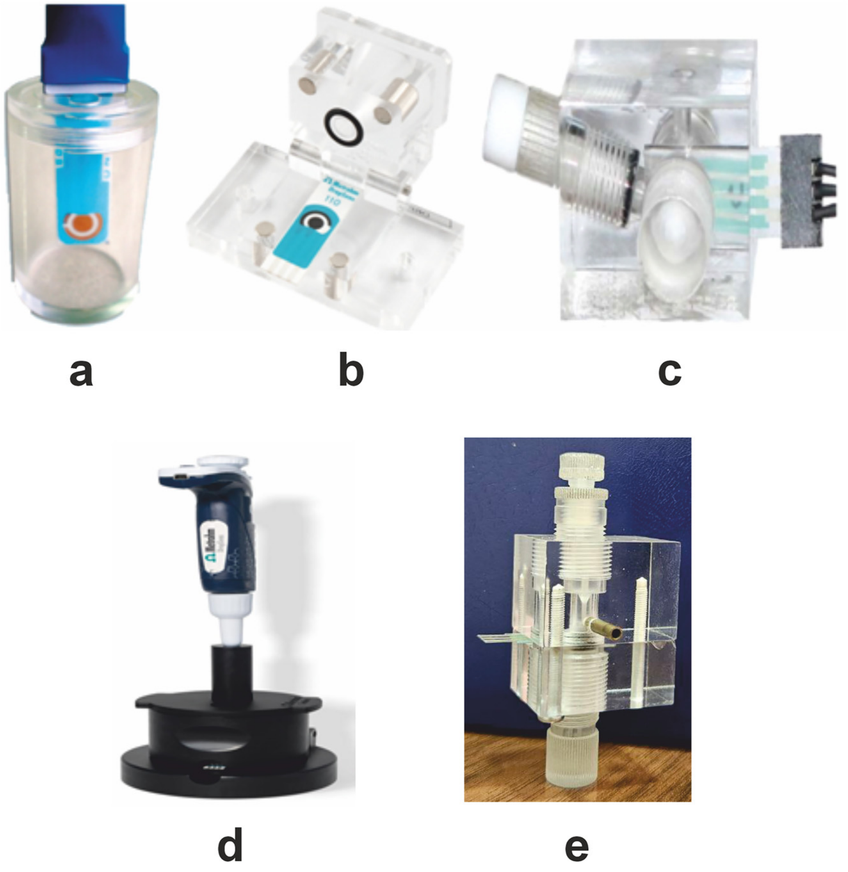

Figure 6: Images of factory-made electrochemical cells for voltammetric analysis using screen-printed electrodes. a) is a stationary mode cell, b) is a DropSens flow-injection cell, c) is a RuSens flow-injection cell, d) batch-injection cell of Ω metrohm, e) batch-injection cell (this work).

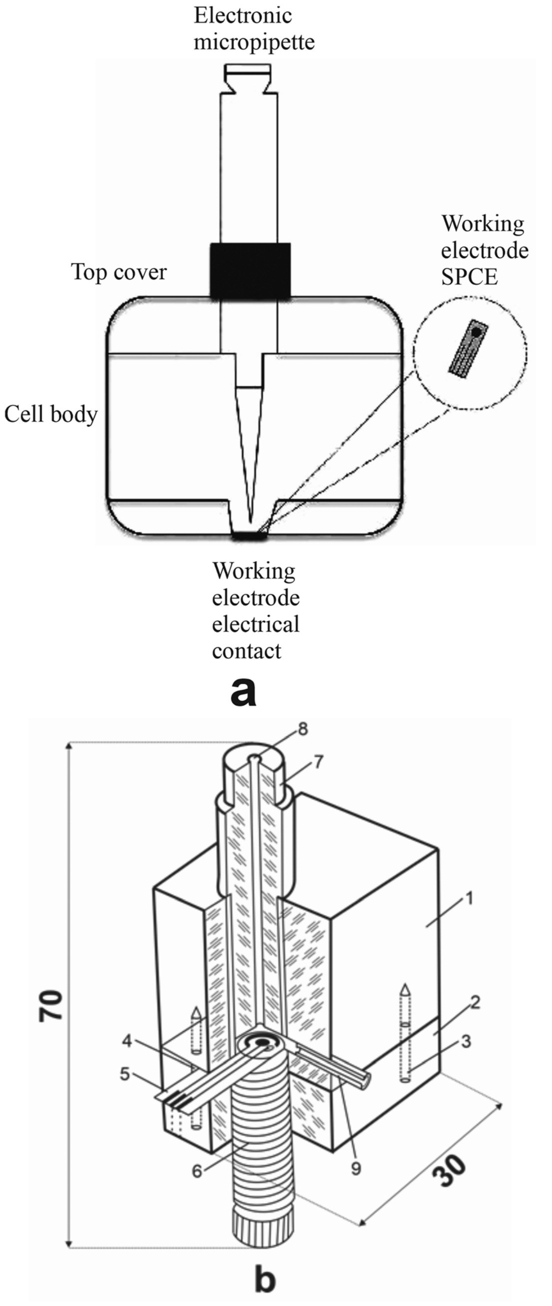

Figure 7: Comparative diagrams of a) the bath-injection cell [74] and b) this work (explanations in the text).

electrochemical cell eliminates the need for a carrier solution supplied by a peristaltic pump. Moreover, the analyzed sample is not diluted during its introduction into the cell.

Thus, the proposed electrochemical cell design is significantly simpler, includes fewer components, lacks moving parts, and is therefore more reliable in operation.

Operation:

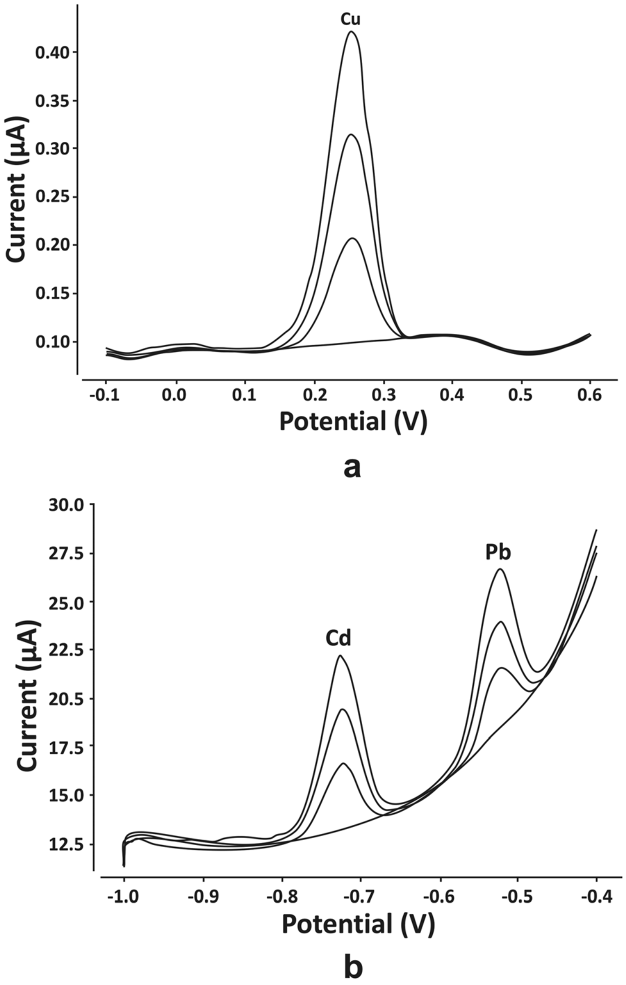

Figure 8: Typical anode voltammograms for Cu(II) and Cd(II), Pb(II) ions obtained on a)Hg-SPCE and b) Bi-SPCE, respectively a) anodic differential pulse voltammogram of Cu(II) ions on the Hg-SPCE in a medium of 0.2 M HCl. Conditions: τ = 30 s, $E_{accum.}$ = −0.5 V; ν = 50 mV/s. Ep. = + 0.25 V. LOD = 0.5 μg L^{-1}. b) Anodic differential pulse voltammogram of Cd(II) and Pb(II) ions on the Bi-SPCE in a medium of 0.1 M Na acetate buffer solution pH 4.5. Conditions: τ = 30 s, $E_{accum.}$ = −1.1 V; ν = 25 mV/s. Ep. = - 0.72 V and – 0.52 V for Cd(II) and Pb(II) ions, respectively. LOD = 10 μg L^{-1}.

A sample prepared for measurement with a volume of 1,000 μl is inserted into the capillary opening of the upper part of the body using a micropipette. The excess solution is drained through the outlet (9). The cuvette is rinsed by injecting distilled water or excess sample volume.

The developed sensor, with modified SPCE, is suitable for analyzing both model and real solutions containing individual metal ions or their mixtures.

Figures 8 and 9 display voltammograms for various ions and electrode types, demonstrating the analytical capabilities of the sensors.

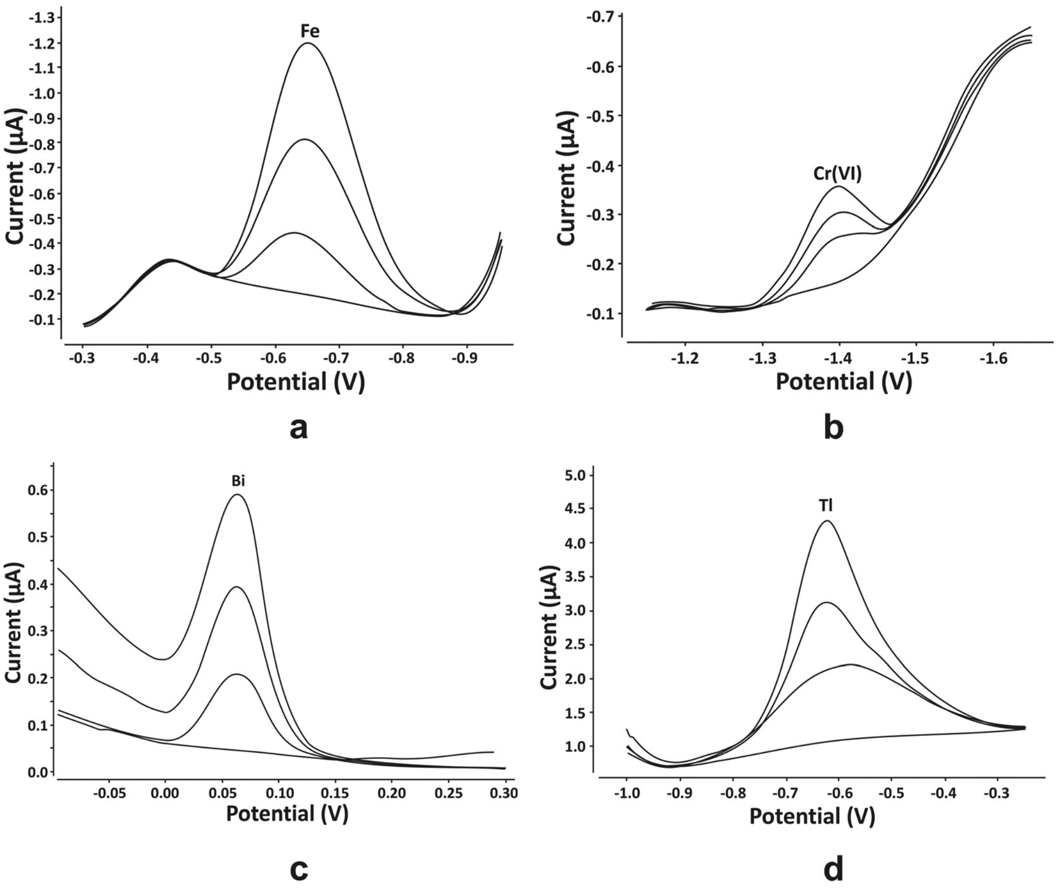

Figure 9: Voltammograms of heavy metal ions obtained at Au-SPCE a) cathodic differential pulse voltammogram of Fe(III) ions on the Au-SPCE in a phosphate buffer solution medium. Conditions: τ = 30 s, E_{accum}. = 0 V;ν = 25 mV/s. in the scanning range −0.3 ÷ −0.95 V; Ep. = – 0.68 V. LOD = 10 μg L^{-1}. b) Cathodic differential pulse voltammogram of Cr(VI) ions on the Au-SPCE in a phosphate buffer solution medium. Conditions: τ = 30 s, E_{accum}. = −1.2 V; ν = 25 mV/s. Ep. = −1.40 V. LOD = 5 μg·L^{-} c) anodic differential pulse voltammogram of Bi(III) ions on the Au-SPCE in a phosphate buffer solution medium. Conditions: τ = 30 s, $E_{accum.}$ = −0.2 V;ν = 25 mV/s in the scanning range −0.2 ÷ + 0.3 V. Ep. = +0.08. LOD = 10 μg L^{-1}. d) Anodic square wave voltammogram of Tl(I) ions on Au-SPCE in a phosphate buffer solution medium. Conditions: τ = 30 s, $E_{accum.}$ = −1.0 V; ν = 25 mV/s in the scanning range −1.0 ÷ – 0.25 V. Ep. = −0.62 V. LOD = 10 μg L^{-1}.

Laboratory studies have shown an adequate response of screen-printed electrodes modified with a thin film of mercury, bismuth and gold to the presence of the corresponding Cu(II), Cd(II), Pb(II), Fe(III), Bi(III) and Cr(VI) ions in solutions and the possibility of using such voltammetry for the analysis of these ions in real samples by the method of standard additions.

The object of the study was water samples from the Zeravshan river, the main source of fresh drinking water for the city of Samarkand and the Samarkand region. Currently, due to the deterioration of the environment and the reduction of water resources suitable for consumption, this river requires constant monitoring for the presence of heavy metal ions and other ecotoxicants in it [75–78].

Water sampling from the Zeravshan river and analytical measurements were carried out jointly with representatives of the analytical laboratory of the Samarkand Regional Department of Ecology, Environmental Protection and Climate Change.

Figure 10 shows a map of the region with the section of the Zeravshan river where the samples were taken, indicating the location of 39°41′43” north latitude and 67°03′15” east longitude.

The control method of analysis was emission spectroscopy performed on an ICP5000 inductively coupled plasma atomic emission spectrometer (Thermo Fisher Scientific, USA).

The measurement results are shown in Table 3.

Field measurements revealed elevated levels of lead, cadmium, chromium, and arsenic compared to acceptable limits, indicating the need for water purification [79–81].

Field measurements, on the one hand, provide faster data collection, and on the other hand, help prevent the effects of chemical changes occurring after sampling, such as the oxidation of arsenic (III) to arsenic (V). An analytical

Figure 10: Map of the Zeravshan river valley showing the location of water sampling.

Table 3: The results of measuring the content of heavy metal ions in the Zeravshan river, conducted in the field.

Determined ion	Type of electrode	Maximum permissible concentrations (MPC) μg·L^{-1} [67]	Found, μg·L^{-1}	AES -ICP μg·L^{-1} $n = 3$; $P = 0.95$
Cu^{2+}	Hg-SPCE	1,000	18.2	17.4 ± 0.08
Pb^{2+}	Bi-SPCE	10	19.8	18.6 ± 0.08
Cd^{2+}	Bi-SPCE	1	8.7	7.6 ± 0.06
Bi^{3+}	Au-SPCE	100	–	0.09 ± 0.02
Tl^{3+}	Au-SPCE	0.1	–	–
As^{3+}	Au-SPCE	10	14.6	13.8 ± 1.02
Fe^{3+}/Fe^{2+}	Au-SPCE	300	28.6	25.7 ± 1.12
Cr^{6+}	Au-SPCE	50	62.3	59.4 ± 2.08

platform utilizing a flow-injection cell and modified screen-printed electrodes is virtually maintenance-free and can meet all field measurement requirements, including real-time and on-site analysis.

4 Conclusions

The study emphasizes the increasing demand for sensitive, selective, and rapid methods for detecting environmental pollutants, particularly heavy metal ions. Among the various detection techniques, electrochemical methods – especially those utilizing screen-printed electrodes (SPE) and microfluidic technologies – offer significant advantages, including high sensitivity, simplicity, and cost-effectiveness. A notable advancement in voltammetry has been achieved through the development of innovative technologies for modifying the surface of screen-printed electrodes with noble metal nanoparticles, their oxides, hexacyanoferrates, organic compounds, and carbon nanomaterials.

In this study, the electrochemical behavior of SPCEs modified with mercury, bismuth, and gold was investigated for the detection of several heavy metal ions in both model and real solutions. These measurements spanned a linear concentration range covering several orders of magnitude, with a detection limit as low as 5 μg per liter.

Furthermore, a novel and ergonomic design for a bath-injection cell compatible with standard SPCEs was developed and tested, enabling real-time voltammetric measurements at the sampling site.

A field trial of this cell with the modified SPCE was conducted to analyze pollution levels in the Zeravshan river, the primary freshwater source for the Samarkand region and surrounding areas. Contamination with lead, cadmium, chromium, and arsenic ions was detected, signaling the urgent need for intervention to improve the environmental conditions in the region.

Notably, the proposed devices enable the measurement of heavy metal ion concentrations under field and expeditionary conditions. These examples demonstrate the promising potential of these technologies to significantly enhance environmental monitoring efforts. Furthermore, they support rapid decision-making, especially in the event of natural or man-made disasters, thereby enabling timely and effective responses.

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