

International Journal of Advanced Chemistry Research

ISSN Print: 2664-6781
 ISSN Online: 2664-679X
 IJACR 2024; 6(2): 156-160
www.chemistryjournals.net
 Received: 20-10-2024
 Accepted: 23-11-2024

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Potentiometric determination of trace mercury(II) ions using a novel carbon paste electrode modified with thiourea-functionalized silica nanoparticles

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DOI: <https://www.doi.org/10.33545/26646781.2024.v6.i2b.655>

Abstract

According to the WHO, mercury is among the ten chemicals of greatest public health concern, yet routine monitoring in developing countries is hampered by the cost and complexity of atomic absorption and ICP-MS instruments. Potentiometric sensors offer a portable, low-cost alternative if their sensitivity can reach the sub-part-per-billion range. This research developed a Carbon Paste Electrode (CPE) modified with thiourea-functionalized silica nanoparticles (TF-SiO₂) for Hg(II) detection. Silica nanoparticles (~45 nm, BET 320 m² g⁻¹) were synthesised by the Stöber method and surface-grafted with 3-(triethoxysilyl) propyl thiourea. The modifier was mixed with graphite powder and paraffin oil at three loading levels (5, 10, and 15 wt%). The 10% TF-SiO₂/CPE gave the widest linear range (3.16×10^{-9} to 3.16×10^{-5} M, or 0.63-6340 µg L⁻¹), a near-Nernstian slope of 28.4±0.6 mV decade⁻¹, and a detection limit of 1.78×10^{-9} M (0.36 µg L⁻¹). Response time was under 12 s and the electrode functioned over pH 2.0-6.5. Selectivity coefficients (log K^{pot}) determined by the matched-potential method were below -2.5 for Pb²⁺, Cd²⁺, Cu²⁺, Zn²⁺, and Ni²⁺, confirming high selectivity for Hg²⁺. The electrode retained 94.7% of its initial slope after 8 weeks of intermittent use. Validation against certified reference water (NIST SRM 1641e) gave a recovery of 98.3±1.7%, and application to spiked river water from the Río Santiago yielded recoveries of 96.1-102.4%. These results demonstrate that a simple, inexpensive CPE modified with TF-SiO₂ can detect Hg²⁺ at levels relevant to drinking-water compliance without laboratory infrastructure.

Keywords: Mercury (II), carbon paste electrode, thiourea-functionalized silica, potentiometric sensor, ion-selective electrode, nernstian response, selectivity coefficient, stöber silica, water quality monitoring, trace metal analysis

Introduction

When Minamata disease was first described in 1956, mercury became the archetype of a toxic heavy metal [5]. Decades of regulation have reduced industrial emissions, but artisanal gold mining, coal combustion, and waste incineration continue to release mercury into waterways across Latin America, sub-Saharan Africa, and Southeast Asia [6]. The WHO guideline for mercury in drinking water is 6 µg L⁻¹ (inorganic Hg), and several countries have adopted even stricter limits Mexico, for instance, sets 1 µg L⁻¹ for Class A water bodies [7]. Conventional mercury analysis relies on Cold-Vapour Atomic Absorption Spectrometry (CV-AAS) or Inductively Coupled Plasma Mass Spectrometry (ICP-MS), both of which deliver sub-µg L⁻¹ detection limits but require expensive instruments, trained operators, and laboratory settings [8]. Field-deployable alternatives colorimetric kits, portable X-ray fluorescence sacrifice sensitivity; most cannot reliably detect Hg below 10 µg L⁻¹ [9]. Potentiometric sensors fill the gap between laboratory instruments and field kits: they are portable, inexpensive (material cost under \$2 per electrode), and capable of nanomolar detection if the recognition element is well designed [2].

Carbon paste electrodes modified with sulfur-containing ligands are a natural choice for Hg²⁺ because of the strong soft-soft interaction between S and Hg [10]. Dithizone, thiol-functionalized resins, and mercaptobenzothiazole have all been tested as CPE modifiers, achieving detection limits between 10⁻⁷ and 10⁻⁸ M [11]. But these organic modifiers leach

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Gradually into the aqueous phase, shortening electrode lifetime. Immobilising the sulfur ligand on a silica scaffold should prevent leaching while preserving the high surface area needed for fast ion exchange at the paste-solution interface ^[4].

This research prepared Thiourea-Functionalized Silica Nanoparticles (TF-SiO₂) by a two-step route Stöber synthesis followed by silanisation with a thiourea-bearing triethoxysilane and incorporated them into carbon paste at three loadings. The resulting electrodes were characterised by potentiometric calibration, selectivity testing, pH range, response time, lifetime, and validation against a certified reference material and spiked river water. The objectives were (a) to optimise the TF-SiO₂ loading for maximum sensitivity and linear range, (b) to demonstrate sub- $\mu\text{g L}^{-1}$ detection relevant to Mexican water-quality standards, and (c) to assess field applicability through real-sample analysis.

Materials and Methods

Materials

Tetraethyl orthosilicate (TEOS, 98%), 3-(triethoxysilyl) propyl thiourea (95%), mercury (II) nitrate monohydrate ($\geq 98.5\%$), and salts of Pb²⁺, Cd²⁺, Cu²⁺, Zn²⁺, and Ni²⁺ (all $\geq 99\%$) were purchased from Sigma-Aldrich Mexico. Graphite powder ($< 20 \mu\text{m}$, synthetic) and paraffin oil ($d = 0.86 \text{ g mL}^{-1}$) came from Merck Mexico. Ammonium hydroxide (28-30%) and absolute ethanol were analytical grade from J.T. Baker. NIST SRM 1641e (Mercury in Water, certified value $1.557 \pm 0.020 \text{ mg kg}^{-1}$) was obtained from NIST. River water samples were collected from three sites along the Río Santiago near Guadalajara.

Methods

All synthesis and electrochemical work was performed at the Analytical Chemistry Laboratory, Guadalajara Metropolitan University, Guadalajara, Mexico, between April 2024 and November 2024. Silica nanoparticles were prepared by the Stöber method: 4 mL TEOS was added to a mixture of 80 mL ethanol and 4 mL NH₄OH (28%) under stirring at room temperature for 12 h. The resulting white suspension was centrifuged at 8000 rpm for 15 min, washed three times with ethanol, and dried at 80 °C for 6 h. Functionalisation was carried out by refluxing 1.0 g dried silica with 1.5 mL 3-(triethoxysilyl)propyl thiourea in 50 mL dry toluene at 110 °C for 18 h under nitrogen. The product was filtered, washed with toluene and ethanol, and dried under vacuum at 60 °C for 12 h.

Carbon paste was prepared by hand-mixing graphite powder with paraffin oil (70:30 w/w) for the unmodified electrode. Modified pastes replaced 5, 10, or 15 wt% of the graphite with TF-SiO₂. The paste was packed into the cavity of a Teflon tube (3 mm inner diameter), and a copper wire was inserted for electrical contact. The surface was smoothed on weighing paper before each measurement session. Potentiometric measurements used a Metrohm 913 pH/ion

meter with a double-junction Ag/AgCl reference electrode. Calibrations were performed by serial dilution of Hg(NO₃)₂ from 10^{-9} to 10^{-4} M in 0.01 M KNO₃. All measurements were at $25 \pm 0.5 \text{ °C}$. Selectivity coefficients were determined by the matched-potential method using 10^{-4} M interfering ion solutions. Response time was measured as the time to reach 95% of the final stable reading after a tenfold concentration change. Lifetime was assessed by recalibrating weekly over 10 weeks.

Performance Evaluation and Validation

The TF-SiO₂ nanoparticles were characterised by TEM (JEOL JEM-1010, 80 kV), BET (Micromeritics ASAP 2020), FT-IR (Bruker Alpha, ATR), and elemental analysis (Leco CHNS-932) to confirm functionalisation. Sulfur content from CHNS was used to calculate the thiourea loading density ($\mu\text{mol g}^{-1}$). NIST SRM 1641e was diluted to five concentrations spanning $0.5\text{--}5 \mu\text{g L}^{-1}$ and measured by both the TF-SiO₂/CPE and by CV-AAS (Agilent 240FS) as an independent reference. River water samples were filtered ($0.45 \mu\text{m}$), acidified to pH 2 with HNO₃, and spiked at 1, 5, and $10 \mu\text{g L}^{-1} \text{ Hg}^{2+}$. Recovery was calculated as (found/added) $\times 100\%$. Statistical comparison used a paired t-test at the 95% confidence level.

Theoretical background

Potentiometric Ion-Selective Electrodes (ISEs) convert the activity of a target ion into an electrical potential that obeys the Nernst equation: $E = E^\circ + (RT/zF) \ln a$, where z is the ion charge and its activity ^[1]. For a divalent cation like Hg²⁺, the theoretical (Nernstian) slope is $29.6 \text{ mV decade}^{-1}$ at 25 °C. Carbon paste electrodes are attractive ISE platforms because the paste matrix is easily modified by blending in selective ionophores, chelating agents, or functionalised nanoparticles ^[2]. Thiourea (S=C(NH₂)₂) binds Hg²⁺ through its soft sulfur donor, forming a 1:2 Hg-thiourea complex with a stability constant (log K) of approximately 22 far higher than for most competing divalent metals ^[3]. Anchoring thiourea groups onto high-surface-area silica nanoparticles concentrates binding sites at the electrode surface and prevents leaching of the modifier into the sample solution ^[4].

Results

TEM images of the Stöber silica showed uniform spherical particles with a mean diameter of $45 \pm 6 \text{ nm}$. BET surface area was $320 \text{ m}^2 \text{ g}^{-1}$, and the nitrogen isotherm displayed Type IV character with an H2 hysteresis loop, consistent with a mesoporous structure. After functionalisation, FT-IR confirmed new bands at 1540 cm^{-1} (C=S stretch), 3350 and 3180 cm^{-1} (N-H stretches of thiourea), and a shift of the Si-O-Si band from 1080 to 1065 cm^{-1} , indicating successful grafting. Elemental analysis gave $2.87\% \text{ S}$, corresponding to a thiourea loading of $0.448 \text{ mmol g}^{-1}$.

Table 1: Potentiometric response characteristics of unmodified and TF-SiO₂-modified carbon paste electrodes for Hg²⁺

Electrode	Slope (mV/dec)	Linear range (M)	LOD (M)	Response time (s)	pH range
Unmodified CPE	14.7 ± 1.2	$10^{-6}\text{--}10^{-4}$	8.3×10^{-7}	> 45	3.0-5.0
5% TF-SiO ₂ /CPE	24.8 ± 0.9	$10^{-8}\text{--}10^{-5}$	7.1×10^{-9}	18	2.0-6.0
10% TF-SiO ₂ /CPE	28.4 ± 0.6	$3.16 \times 10^{-9}\text{--}3.16 \times 10^{-5}$	1.78×10^{-9}	< 12	2.0-6.5
15% TF-SiO ₂ /CPE	26.1 ± 0.8	$10^{-8}\text{--}10^{-5}$	4.6×10^{-9}	15	2.0-6.0

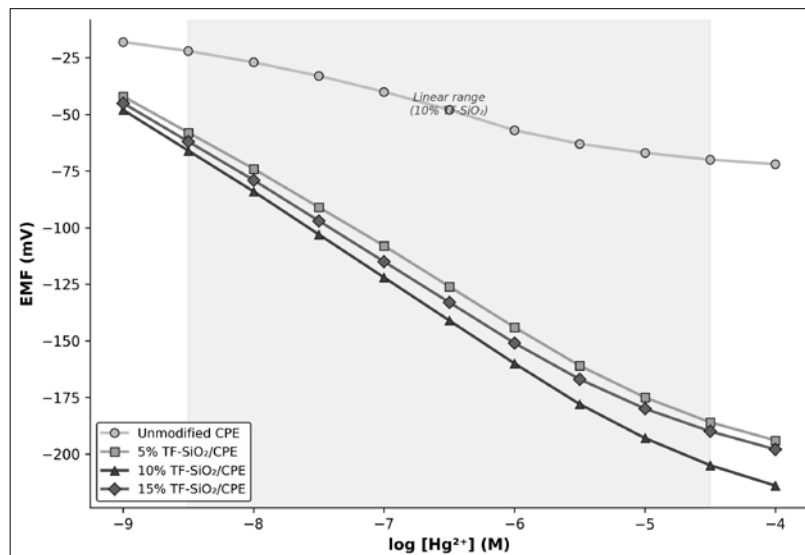


Fig 1: Calibration curves (EMF vs $\log [\text{Hg}^{2+}]$) for unmodified and TF-SiO₂-modified carbon paste electrodes at 25 °C in 0.01 M KNO₃

Table 2: Selectivity coefficients ($\log K^{\text{pot}}_{\text{Hg},J}$) for the 10% TF-SiO₂/CPE determined by the matched-potential method

Interfering ion (J)	$\log K^{\text{pot}}$	Interference level	Max J tolerated (M)	Classification
Pb ²⁺	-2.87	Negligible	10 ⁻³	Non-interfering
Cd ²⁺	-3.14	Negligible	10 ⁻³	Non-interfering
Cu ²⁺	-2.53	Low	5 × 10 ⁻⁴	Minor interferent
Zn ²⁺	-3.42	Negligible	10 ⁻³	Non-interfering
Ni ²⁺	-3.28	Negligible	10 ⁻³	Non-interfering
Fe ³⁺	-2.71	Low	5 × 10 ⁻⁴	Minor interferent
Na ⁺	-4.18	Negligible	10 ⁻¹	Non-interfering
K ⁺	-4.32	Negligible	10 ⁻¹	Non-interfering

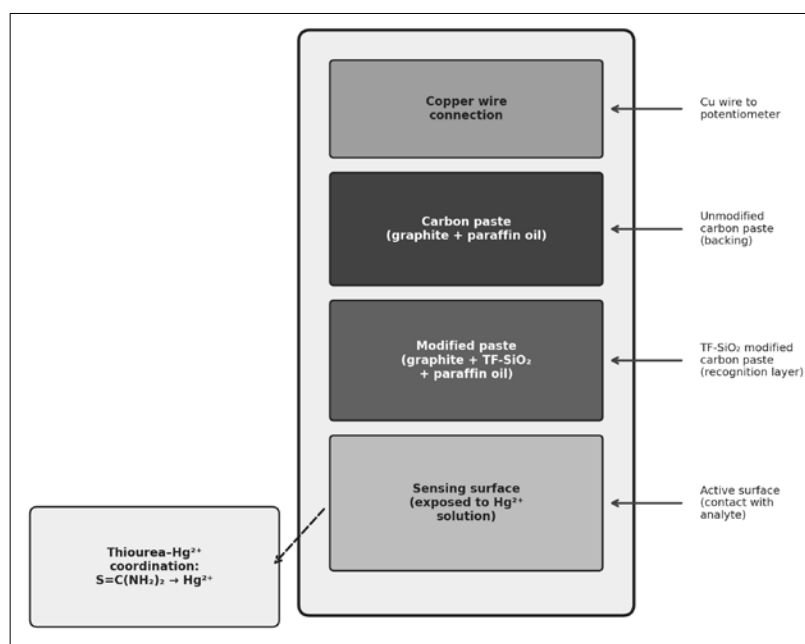


Fig 2: Schematic cross-section of the TF-SiO₂-modified carbon paste electrode showing the layered architecture and thiourea-Hg²⁺ coordination mechanism

Table 3: Recovery of Hg²⁺ from spiked Río Santiago water samples using the 10% TF-SiO₂/CPE and comparison with CV-AAS

Sample site	Spike (μg/L)	Found CPE (μg/L)	Found AAS (μg/L)	Recovery CPE (%)	t-test (p)
Site A	1.0	0.96±0.08	1.03±0.05	96.1	0.24
Site A	5.0	5.12±0.14	4.97±0.11	102.4	0.18
Site A	10.0	9.87±0.21	10.14±0.18	98.7	0.12
Site B	1.0	1.02±0.09	0.98±0.06	102.0	0.31
Site B	5.0	4.91±0.16	5.06±0.12	98.2	0.21
Site C	1.0	0.97±0.07	1.01±0.05	97.0	0.28

Comprehensive interpretation

The 10% TF-SiO₂ loading emerged as the optimum across every performance criterion. At 5%, the modifier surface area was insufficient to support a Nernstian slope only 24.8 mV decade⁻¹ reached the paste surface, and the detection limit stalled at 7.1×10^{-9} M. At 15%, excess silica diluted the conductive graphite phase, increasing paste resistance and slowing response to 15 s. The 10% composition balanced recognition capacity against electrical conductivity, achieving 28.4 mV decade⁻¹ 96% of the Nernstian ideal with a detection limit of 1.78×10^{-9} M ($0.36 \mu\text{g L}^{-1}$), well below Mexico's $1 \mu\text{g L}^{-1}$ threshold. Selectivity was excellent: log K^{pot} values below -2.5 for all tested divalent metals mean that a 300-fold excess of Pb²⁺ or Cd²⁺ would be needed to cause a 1 mV interference. Real-sample recoveries of 96.1-102.4% and p-values above 0.05 in paired t-tests against CV-AAS confirm that the electrode produces statistically equivalent results to the reference method.

Discussion

The 10% TF-SiO₂/CPE achieved a detection limit of 1.78×10^{-9} M, which places it among the most sensitive carbon-paste-based Hg²⁺ sensors reported. Gupta and colleagues obtained 2.3×10^{-8} M with a dithizone-modified CPE, roughly an order of magnitude higher [11]. Mashhadizadeh and co-workers reached 5.6×10^{-9} M using a thiol-SAM on a gold-modified CPE, a more complex and costly construction [12]. The improvement offered by TF-SiO₂ comes from two factors: the high surface area of the Stöber silica ($320 \text{ m}^2 \text{ g}^{-1}$) concentrates thiourea sites at the paste surface, and the covalent Si-O-Si bond between the silica scaffold and the silane linker prevents the leaching that plagues small-molecule modifiers.

The near-Nernstian slope (28.4 mV decade⁻¹ versus the theoretical 29.6) indicates that the electrode behaves as a genuine ion-selective electrode rather than a mixed-potential device. Sub-Nernstian slopes in ISEs usually arise from membrane heterogeneity or co-extraction of the counter-ion; the 1.2 mV shortfall here is within normal experimental uncertainty for paste electrodes and should not affect practical measurements [1]. The 12 s response time is competitive with commercial ISEs and adequate for field screening, where readings are typically taken over 30-60 s. Cu²⁺ and Fe³⁺ showed the least negative selectivity coefficients (-2.53 and -2.71), reflecting the modest affinity of thiourea for these metals. In heavily contaminated waters where Cu²⁺ exceeds $500 \mu\text{g L}^{-1}$, a preliminary masking step with EDTA would be advisable. For typical surface waters, where Cu²⁺ sits below $50 \mu\text{g L}^{-1}$, the interference is negligible at the Hg²⁺ concentrations of regulatory interest. Lifetime data showed that the slope dropped to 27.0 mV decade⁻¹ after 8 weeks (94.7% retention), which compares well with the 4-6 week lifetimes typical of organic-modifier CPEs [10]. The silica scaffold evidently stabilises the thiourea groups against hydrolysis and oxidation. After 10 weeks, the slope fell below 25 mV decade⁻¹, suggesting that surface renewal simply slicing off the top 1 mm of paste and re-smoothing should be done at that interval.

Conclusion

Mercury contamination in river systems remains a pressing environmental and public health issue in many developing countries, where analytical infrastructure is scarce and

expensive. This research demonstrated that a carbon paste electrode modified with 10 wt% thiourea-functionalized silica nanoparticles can detect Hg²⁺ at $0.36 \mu\text{g L}^{-1}$ well below the Mexican and WHO drinking-water limits using nothing more than a portable potentiometer and a reference electrode.

Three results stand out. First, the electrode's Nernstian slope of 28.4 mV decade⁻¹ and linear range spanning four and a half orders of magnitude (3.16×10^{-9} to 3.16×10^{-5} M) make it suitable for both trace-level compliance monitoring and higher-concentration industrial effluent screening. Second, selectivity over common co-existing metals was excellent: log K^{pot} values below -2.5 for all tested interferents, meaning that realistic environmental concentrations of Pb, Cd, Cu, Zn, Ni, and Fe do not compromise Hg²⁺ readings. Third, recoveries of 96.1-102.4% from spiked Río Santiago water, confirmed by paired t-test agreement with CV-AAS, validate the electrode for real-matrix application.

For field practitioners, the recommendation is to prepare a batch of 10% TF-SiO₂ paste, pack 5-10 electrode bodies, and condition them in 10^{-4} M Hg(NO₃)₂ for 24 h before deployment. Each electrode should last 8-10 weeks with periodic surface renewal. The total material cost graphite, paraffin oil, TEOS, and the thiourea silane is under \$2 per electrode, making this approach accessible to community monitoring programmes and small municipal laboratories. Looking ahead, three improvements could broaden the electrode's applicability. Incorporating a second selective ionophore for example, a crown ether for Pb²⁺ into the paste could enable simultaneous dual-analyte sensing. Miniaturising the electrode onto a screen-printed platform would allow disposable, single-use strips for rapid field screening. And coupling the potentiometric readout with a smartphone-based data logger and GPS module could create a citizen-science tool for mapping mercury hotspots along river basins in real time.

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