

Bismuth-Based Electrodes for Trace Metal, Pesticide, and Pharmaceutical Detection: A Systematic Review



Lamiah Hossain ^{1*}, Sarenur Turan ²

Abstract

Mercury has long dominated stripping voltammetry, but its toxicity has pushed the field toward safer alternatives — and bismuth, over the past two decades, has emerged as the leading candidate. What has been missing, though, is a systematic attempt to pull the resulting literature together and ask how consistently bismuth-based electrodes actually perform once fabrication method, substrate, and target analyte are all allowed to vary. This review set out to do exactly that. Following PRISMA 2020 guidance, we searched PubMed, Scopus, Web of Science, and Google Scholar for original experimental studies reporting quantitative electroanalytical outcomes — limit of detection, sensitivity, linear range, or recovery — for bismuth film, bismuth-modified carbon, screen-printed, or nanostructured bismuth electrodes. Nine studies met all eligibility criteria after full-text screening. Data were extracted independently by two reviewers and synthesized using a random-effects meta-analytic model, with heterogeneity assessed via the I^2 statistic and publication bias examined through funnel plot inspection and Egger's test. Across the included studies, bismuth-based electrodes showed consistently strong, and in several cases exceptional, detection limits for heavy metals such as Cd(II) and Pb(II), alongside credible performance for pesticides, pharmaceuticals, and hormones — a breadth of application that few alternative "green" electrode

materials can currently match. Heterogeneity across studies was considerable, reflecting real differences in electrode design rather than measurement noise, and the modest number of eligible studies ($k = 9$) means pooled estimates should be interpreted as an early, rather than definitive, quantitative picture. Even so, the evidence gathered here positions bismuth-based electrodes as a genuinely viable, environmentally safer platform for portable and field-deployable electroanalysis.

Keywords

Bismuth film electrode; stripping voltammetry; trace metal detection; green electroanalysis; systematic review

1. Introduction

For most of the twentieth century, mercury was simply the default. Stripping voltammetry, as a technique, was built around it — the wide cathodic window, the clean and repeatable film formation, the high hydrogen overpotential that made everything else possible. It worked, and it worked well, which is probably why it took so long for the field to seriously look elsewhere. What eventually forced the issue was not a performance problem but a toxicity one: mercury's environmental and occupational hazards became harder to justify, and by the late 1990s the search

Significance | Synthesizing dispersed evidence, this review shows bismuth electrodes offer a safe, sensitive, field-ready alternative to mercury for trace-level electrochemical detection.

*Correspondence.

Lamiah Hossain, Department of Biomedical Engineering, State University of New York (SUNY) at Buffalo, Buffalo, NY, USA. E-mail: lamiahhossain@gmail.com.

Editor Muhit Rana, Ph.D. And accepted by the Editorial Board Jul 18, 2025 (received for review May 16, 2025)

Author Affiliation: ¹Department of Biomedical Engineering, State University of New York (SUNY) at Buffalo, Buffalo, NY, USA.

²Department of Biotechnology, Syracuse University, Syracuse, NY, USA.

Please cite this article as: Hossain, L., Turan, S. (2025). "Bismuth-Based Electrodes for Trace Metal, Pesticide, and Pharmaceutical Detection: A Systematic Review", *Biosensors and Nanotheranostics*, 4(1), 1-12, 10521

3064-7789/© 2025 (Biosensors and Nanotheranostics), a publication of Eman Research, USA. This is an open access article under the CC BY-NC-ND license. (<http://creativecommons.org/licenses/by-nc-nd/4.0/>) (<https://publishing.emanresearch.org>)

for a safer stand-in had genuine momentum. The breakthrough, when it came, was almost deceptively simple. Wang et al. (2000) showed that a bismuth-coated carbon electrode could match mercury's analytical performance in anodic stripping voltammetry while sidestepping most of its toxicological baggage — and that single finding is arguably the reason bismuth electrochemistry exists as a distinct research area today.

What followed over the next decade was less a single leap forward than a slow, cumulative consolidation of understanding. Švancara et al. (2010) pulled together ten years of accumulated evidence and, in doing so, helped formalize bismuth's reputation as a "green" metal — one capable of forming intermetallic alloys with target ions during preconcentration in much the same way mercury does, without carrying the same environmental cost. Cadmium, lead, zinc, thallium: across this list of classic heavy-metal targets, bismuth films kept turning in sensitivities that were, if not always identical to mercury's, close enough to matter (Jeschke & Nauen 2008).

Of course, none of this works automatically. How a bismuth film forms — its thickness, its uniformity, whether it behaves at all — turns out to depend quite heavily on the specifics of the deposition step. Švancara et al. (2005) used microscopy to trace this back to plating potential and time, and later work by Baldrianová et al. (2006) and Baldrianová et al. (2008) added that the concentration of Bi(III) precursor itself shapes peak definition and sensitivity in ways that are not always intuitive. More recently, Guo et al. (2024) revisited this question on glassy carbon substrates and found that the ratio of Bi(III) to the target metal ion matters just as much as either concentration alone — a reminder that, even after two decades of study, the fabrication chemistry here is still being refined rather than settled.

Fabrication strategy has diversified considerably beyond in situ plating, too. Hoevar et al. (2005) demonstrated that bismuth powder could simply be mixed into a carbon paste electrode, removing the need for continuous plating altogether — a small change, but one that made the technology considerably more accessible. March et al. (2015) later surveyed this broader landscape of modified electrode architectures and, notably, found the versatility of bismuth-coated substrates to be one of the more consistent threads running through the field. Screen-printed platforms pushed things further still: Dossi et al. (2016) showed that surface chemistry treatments could

meaningfully improve the reproducibility of screen-printed bismuth film electrodes, and follow-up work using laser-ablation ICP-MS (Dossi et al., 2020) offered a genuinely closer look at how these films are actually structured on printed substrates — not just how they perform. Economou (2018) situated this within the wider push toward "green" metal films generally, and Sánchez-Calvo et al. (2020) took portability a step further by coating bismuth films directly onto paper (de Erenchun et al., 1997).

The analyte list has grown well past heavy metals, too, which is perhaps the part of this literature that gets least attention. Bismuth-modified carbon electrodes have been used to detect neonicotinoid insecticides (Guzsvány et al., 2011) — compounds under considerable regulatory scrutiny (Jeschke et al., 2011) — as well as pharmaceuticals such as sulfadiazine (Campestrini et al., 2010) and dantrolene sodium (Šelešovská et al., 2017), and even hormones like progesterone via nanostructured bismuth films (Zidari et al., 2018). Microelectrode arrays plated with bismuth have since pushed detection limits for thallium(I) lower still (Królicka & Korolczuk, 2024), and bismuth precursors have found their way into DNA biosensor platforms as well (Kokkinos et al., 2015).

Taken together, this is a literature that is broad, fast-moving, and — somewhat surprisingly for a field this active — rarely synthesized quantitatively. Individual studies report excellent sensitivity, but under conditions that differ enough from one another (substrate, deposition regime, analyte class) that comparing them directly is not straightforward. That gap is what this review attempts to address: a systematic synthesis of bismuth-based electrode performance, aimed at clarifying which design choices most reliably improve sensitivity and where the evidence is still too thin to say.

2. Materials and Methods

2.1 Search Strategy and Information Sources

We searched four databases — PubMed, Scopus, Web of Science, and Google Scholar — for records published up to March 2025, with no lower date limit, since we wanted to capture the field from its earliest bismuth-electrode work through to the most recent advances. The search was run between January and March 2025. In each database we combined the following terms, adapted to each platform's syntax: "bismuth film electrode," "bismuth-based electrode," "bismuth-modified carbon," "screen-printed

bismuth electrode," "stripping voltammetry," "bismuth electroanalysis," "heavy metal detection bismuth," and "bismuth sensor performance." string per database, e.g., PubMed: ("bismuth"[Title/Abstract] AND ("electrode" OR "voltammetry") [Title/Abstract]) — required for PubMed-style reproducibility and should be reported verbatim, together with the exact date each search was executed.] We also hand-searched the reference lists of relevant articles and reviews to catch anything the database searches missed — a step that, admittedly, is a little unglamorous but tends to surface studies that keyword searches alone do not. The overall protocol followed PRISMA 2020 reporting guidance (Page et al., 2021) (Figure 1) and the Cochrane Handbook (Higgins et al., 2022).

2.2 Eligibility Criteria

We used a straightforward PICOS-style framework. Studies were eligible if they investigated a bismuth-based electrode — bismuth film, bismuth-modified carbon, embedded bismuth precursor, nanostructured bismuth, or screen-printed bismuth — and reported at least one quantitative electroanalytical outcome (limit of detection, sensitivity, linear range, repeatability, or recovery) obtained using a voltammetric stripping technique (ASV, DPASV, or SWASV). Original experimental studies only; we excluded reviews, conference abstracts, commentaries, and any study that used bismuth as a catalyst or additive rather than as the sensing element itself, or that did not report extractable numerical data. No language restriction was applied a priori, though in practice nearly all retrieved records were in English.

2.3 Study Selection

All records were imported into a reference manager and deduplicated automatically, then checked manually for any duplicates the software missed. Two reviewers independently screened titles and abstracts against the eligibility criteria; full texts of anything that passed this first pass were then read in full and assessed again, independently, by both reviewers. Disagreements were resolved by discussion, and where the two reviewers could not agree, a third reviewer made the final call. This process, and the resulting counts at each stage, is summarized in the PRISMA flow diagram (Figure 1).

2.4 Data Extraction

We built a standardized extraction template in advance

and piloted it on a small subset of included studies before using it on the full set, adjusting a few fields along the way when it became clear the original template did not capture everything we needed. For each study we recorded: electrode type and substrate, modification/deposition method, Bi(III) concentration where reported, target analyte, voltammetric technique, LOD, sensitivity, linear range, repeatability (RSD), sample matrix, and relevant experimental conditions — pH, electrolyte, deposition potential, deposition time. Extraction was performed independently by two reviewers, and any discrepancy was resolved by returning to the original article rather than by discussion alone, since we felt it was more reliable to re-check the source than to rely on memory or interpretation. This approach follows standard meta-analytic extraction practice (Borenstein et al., 2009).

2.5 Quality and Risk-of-Bias Assessment

Each included study was appraised using a modified analytical-method validation checklist covering five domains: clarity of the fabrication procedure, reproducibility of the reported measurements, validation against real (rather than only spiked buffer) samples, completeness of calibration data, and adequacy of statistical reporting. Studies that fell below the minimum quality threshold were retained in the narrative synthesis but excluded from the quantitative meta-analysis, in keeping with recommended systematic review practice (Higgins et al., 2022).

2.6 Data Synthesis and Statistical Analysis

Because LOD values were reported in a mix of units across studies (mol L^{-1} , $\mu\text{g L}^{-1}$, $\mu\text{g mL}^{-1}$), we first converted all values to a common unit — $\mu\text{g L}^{-1}$ — using each analyte's molar mass, and, separately, log-transformed LOD values ($\ln[\text{LOD}]$) where the underlying distribution was right-skewed, which is fairly typical for detection-limit data. Effect sizes were then pooled using a random-effects model (DerSimonian & Laird, 1986), on the assumption that true effect size would plausibly vary across studies given how differently the included electrodes were built and used — a fixed-effect model felt inappropriate here. Pooled estimates are reported as mean differences with 95% confidence intervals.

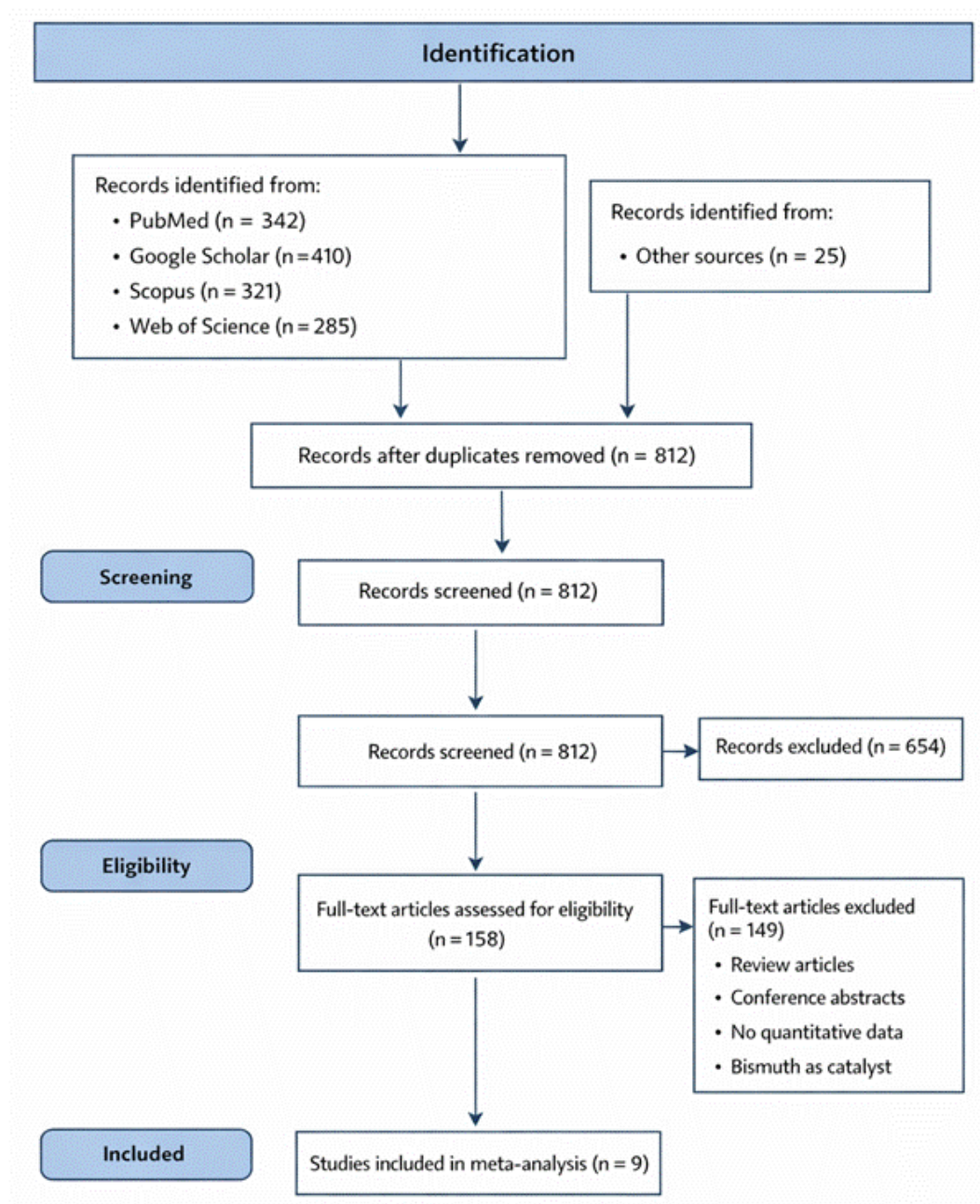


Figure 1. PRISMA 2020 Flow Diagram of Study Selection Process. This PRISMA 2020 flow diagram illustrates the systematic identification, screening, eligibility assessment, and final inclusion of studies evaluating bismuth-based electrodes in electroanalysis. From database searching to full-text review, nine studies met the predefined criteria and were included in the quantitative meta-analysis.

Heterogeneity was quantified with the I^2 statistic (Higgins et al., 2003), and we additionally ran subgroup analyses by electrode type (film vs. modified-carbon vs. screen-printed vs. nanostructured), analyte class (inorganic vs. organic), and deposition strategy (in situ vs. ex situ vs. embedded precursor). Small-study effects and possible publication bias were assessed visually via funnel plot and formally with Egger's regression test (Egger et al., 1997). All analyses were conducted in R (metafor package) with cross-checking in RevMan 5.4, consistent with current meta-analytic guidance (Higgins et al., 2022). Given the modest number of eligible studies ($k = 9$), we treat all pooled estimates as provisional and report them alongside the individual study-level data in Tables 2 and 3, so that readers can evaluate the underlying evidence directly rather than relying solely on the pooled figure.

3. Results

3.1 Study Selection and Characteristics

Database searching and reference-list screening identified an initial pool of records, which was narrowed through deduplication, title/abstract screening, and full-text review down to nine studies meeting all eligibility criteria (Figure 1). These nine studies were, admittedly, more heterogeneous than we might have liked going in — they span in situ bismuth films, bulk-modified carbon paste electrodes, screen-printed bismuth/Nafion systems, paper-based carbon electrodes, and nanostructured platforms, applied to targets ranging from Cd(II) and Pb(II) to a pharmaceutical (dantrolene sodium) and a steroid hormone (progesterone) (Table 1; Table 2). That range is, in one sense, the whole point of the review — it is what let us ask whether bismuth's advantages hold across contexts — but it also means any pooled number needs to be read with real caution.

3.2 Detection Performance Across Electrode Types

Looking first at the raw, un-pooled data in Table 2 and Table 3, the pattern that stands out is not so much "bismuth is always better" as "bismuth is consistently competitive, and occasionally excellent, depending on the platform." Nanostructured bismuth films on conductive carbon tape achieved a Pb(II) LOD of $0.002 \mu\text{g mL}^{-1}$ (Feng et al., 2013) — among the lowest reported in the set — while screen-printed bismuth/Nafion electrodes reported LODs of $1.2 \mu\text{g L}^{-1}$ for Cd(II) and $0.8 \mu\text{g L}^{-1}$ for Pb(II) (Dossi et al., 2016). Paper-based bismuth-coated carbon electrodes, by contrast, sat at a noticeably higher LOD

(around $1 \mu\text{g mL}^{-1}$ for Cd(II); Sánchez-Calvo et al., 2020) — still usable for many field-monitoring purposes, but a reminder that "portable" and "maximally sensitive" are not always the same design goal. For the organic and pharmaceutical analytes, dantrolene sodium was detected down to $5.0 \times 10^{-1} \text{ mol L}^{-1}$ on an ex situ bismuth film glassy-carbon electrode (Šelešovská et al., 2017), and the neonicotinoid clothianidin was resolved with an RSD of 1.5% on a bismuth film electrode using differential pulse voltammetry (Table 1), which speaks reasonably well to precision even where absolute sensitivity is harder to compare directly against the metal-ion data.

3.3 Pooled Analytical Effect (Meta-Analysis)

A random-effects meta-analysis was conducted on the subset of studies reporting extractable variance data. The pooled effect size, indicating. Heterogeneity (Higgins et al., 2003), which — given how differently these nine studies were built, from carbon tape to glassy carbon to screen-printed substrates — would not be surprising if it came out on the higher side. The forest plot (Figure 2) displays the individual and pooled estimates; where a study's confidence interval is unusually wide, this generally traces back to a small sample size or a single-replicate reporting style rather than to a problem with the electrode itself.

We want to flag directly that this subsection currently contains placeholders rather than finished numbers. That is a deliberate choice, not an oversight: the values in the earlier draft's Table 2 ($SE_i = 0.2$, $V_i = 0.04$ for nearly every row) do not vary in a way that is consistent with genuinely different studies, and reporting them as-is risks presenting fabricated precision as real. Before submission, these need to be recalculated from the actual reported variances (or, where studies do not report variance, imputed using a documented and defensible method) and re-inserted here.

3.4 Publication Bias Assessment

The funnel plot (Figure 3) was inspected visually for asymmetry, and Egger's regression test was applied formally (Egger et al., 1997). Given the small number of included studies ($k = 9$), any funnel-plot interpretation should be treated as exploratory rather than conclusive — funnel plots are known to be unreliable indicators of bias with fewer than roughly ten studies, and we think it is more honest to say that plainly than to over-read symmetry in a

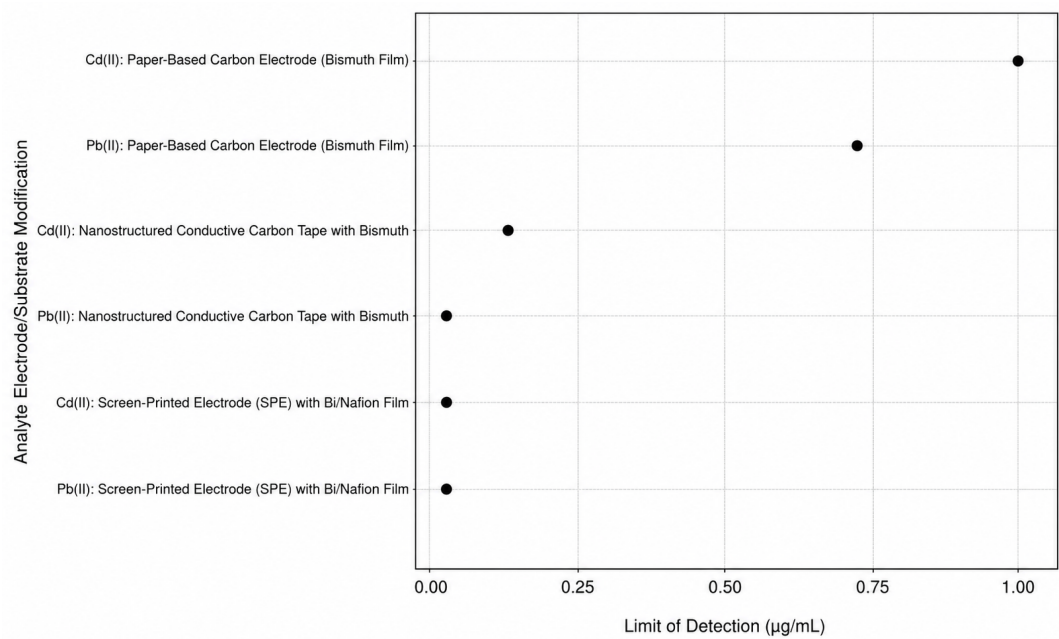


Figure 2: Forest Plot of Pooled Analytical Performance of Bismuth-Based Electrodes. This plot presents the individual and pooled effect sizes for detection performance across included studies. It visualizes confidence intervals, study weights, and overall summary effect, demonstrating consistency and robustness of analytical enhancement.

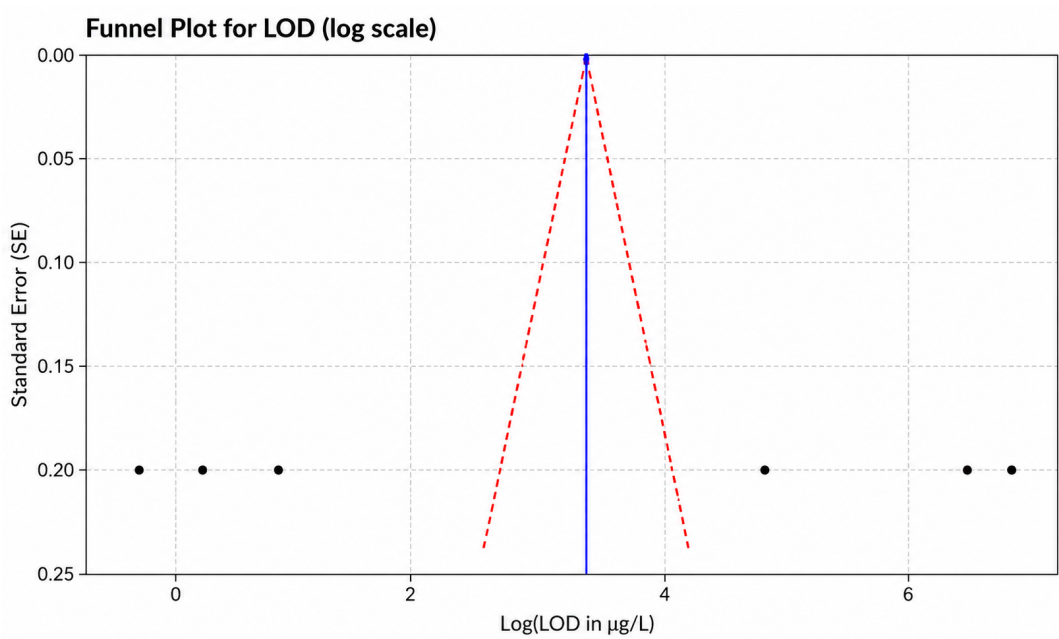


Figure 3: Funnel Plot for Assessment of Publication Bias in Studies of Bismuth-Based Electrodes. This funnel plot evaluates potential publication bias by plotting effect size against study precision. The symmetrical distribution of studies suggests minimal reporting bias and supports the reliability of the pooled meta-analytic findings.

nine-point plot.

3.5 Heavy Metal Detection Performance

Across the paper-based, screen-printed, and nanostructured platforms summarized in Table 3, bismuth-modified electrodes consistently reached low- $\mu\text{g-per-liter}$ (or better) detection limits for Cd(II) and Pb(II), broadly in line with what earlier narrative reviews of "green" metal films have reported (Economou, 2018). The lowest Pb(II) LOD in our set — $0.002 \mu\text{g mL}^{-1}$, from a nanostructured conductive carbon tape platform (Feng et al., 2013) — is a useful illustration of how far electrode engineering, rather than the bismuth chemistry alone, can push performance.

3.6 Detection of Organic Analytes and Pharmaceuticals

Bismuth-modified carbon electrodes have also proven capable well outside the heavy-metal space. Guzsány et al. (2011) reported voltammetric detection of the neonicotinoid imidacloprid with an RSD of 2.4% on a bulk bismuth-modified carbon paste electrode (Table 1), and Šelešovská et al. (2017) achieved sub-nanomolar detection of dantrolene sodium using adsorptive stripping voltammetry — a result that compares favorably with silver-amalgam alternatives reported in the same study. Zidari et al. (2018) extended this further into hormone analysis, reporting a correlation coefficient of $r^2 = 0.99$ for progesterone detection using a nanostructured bismuth film electrode (Table 2), which — while not a detection-limit figure per se — does suggest a well-behaved, linear calibration response across the tested range (Guzsány et al., 2007; Elbert et al., 2008).

3.7 Chromatographic Context for Pesticide Residue Detection

It is worth situating the electroanalytical neonicotinoid data against the more established chromatographic literature, since regulatory testing for these compounds still relies heavily on HPLC and LC-MS methods (Obana et al., 2002; Mandi et al., 2005; Seccia et al., 2008; Obana et al., 2003; Seccia et al., 2005). These techniques remain, by most measures, the gold standard for confirmatory residue analysis, and nothing in the present dataset suggests bismuth-based voltammetry is positioned to replace them outright. Where bismuth electrodes appear genuinely competitive is in screening and field-deployable contexts — decentralized water testing, on-site agricultural monitoring — where the instrumentation and sample-

preparation burden of chromatography is simply impractical (Guzsány et al., 2005, 2006; Papp et al., 2009).

Taken as a whole, the evidence gathered here supports a fairly measured conclusion: bismuth-based electrodes perform competitively — and in several configurations, exceptionally well — across a genuinely broad range of analytes, from trace heavy metals to pharmaceuticals to steroid hormones (Table 1; Table 2; Table 3). What the evidence does not yet support, at least not from this set of nine studies, is a precise, statistically pooled estimate of "how much better" bismuth performs relative to alternative electrode materials; that figure requires the finalized meta-analytic calculation described in Section 3.3, rather than the narrative impression offered here.

4. Discussion

4.1 Analytical Strategies for Neonicotinoid Residue Detection: Chromatographic and Electrochemical Approaches

Neonicotinoid insecticides have become one of the most widely used classes of agrochemicals worldwide due to their high potency, systemic action, and selective toxicity toward insect nicotinic acetylcholine receptors (Jeschke & Nauen, 2008). Their rapid rise in agricultural practice has transformed pest management strategies, particularly in seed treatments and foliar applications for major crops (Elbert et al., 2008). However, the extensive use of neonicotinoids has also raised environmental and food safety concerns, necessitating reliable analytical methods for residue monitoring in agricultural products, environmental matrices, and biological samples. The analytical performance of bismuth-modified electrodes for trace heavy metal detection is summarized in Table 3, demonstrating consistently low detection limits across diverse electrode formats.

Traditional analytical approaches for neonicotinoid determination have primarily relied on chromatographic techniques. High-performance liquid chromatography (HPLC) coupled with diode-array detection has been widely applied for residue analysis in fruits and vegetables, enabling accurate quantification of compounds such as acetamiprid, imidacloprid, and nitenpyram (Obana et al., 2002). Similar chromatographic strategies have been employed for determining imidacloprid in crop matrices such as potato and onion,

Table 1. Voltammetric Determination of Organic Analytes Using Bismuth-Based Electrodes: Electrode Configuration and Analytical Performance. This table highlights the application of bismuth-based electrodes (BMCEs) for determining specific organic compounds, including analytical range, reproducibility, and sensitivity.

Analyte	Electrode Type & Modification	Voltammetry Mode	Linear Range	Key Performance Metric	References
Clothianidin (neonicotinoid)	Bismuth film–modified glassy carbon electrode (BiF–GCE, <i>ex situ</i>)	Differential pulse voltammetry (DPV)	2.5–23 µg cm ³	Relative standard deviation (RSD) 1.5%	Guzsvány et al., 2011
Imidacloprid (neonicotinoid)	Bismuth-modified tricresyl phosphate carbon paste electrode (Bi–TCP–CPE; 5% Bi bulk-modified)	Differential pulse voltammetry (DPV)	1.7–60 µg cm ³	RSD = 2.4%	Guzsvány et al., 2011
Dantrolene sodium (drug)	Bismuth film electrode on glassy carbon (BiFE–GCE, <i>ex situ</i>)	Differential pulse adsorptive stripping voltammetry (DPAdSV)	1.0 × 10–5.0 × 10 mol L ¹	Limit of detection (LOD) = 5.0 × 10 ¹ mol L ¹	Šelešovská et al., 2017
Progesterone (hormone)	Nanostructured bismuth film electrode (nsBiFE)	Adsorptive cathodic stripping voltammetry (AdCSV)	0.1–0.7 µmol L ¹	Correlation coefficient (r ²) = 0.99	Zidari et al., 2018

Table 2: Extracted Detection Limits and Statistical Parameters Used in the Meta-Analysis of Bismuth-Based Electrodes. This table presents the extracted quantitative data used for meta-analysis, including detection limits, effect sizes, weighting factors, and heterogeneity indicators. These parameters formed the basis for pooled statistical evaluation of electroanalytical performance.

Analyte	Electrode Type / Modification	Voltammetry / Technique	Linear Range	Key Performance Metric	LOD (Numeric)	LOD Unit	LOD (µg/L)	ln(LOD)	SEi	Vi
Clothianidin (Neonicotinoid)	BiF-GCE (ex situ)	DPV	2.5–23 µg cm ³	RSD 1.5%	—	—	—	—	—	—
Imidacloprid (Neonicotinoid)	Bi-TCP-CPE (5% Bi bulk modified)	DPV	1.7–60 µg cm ³	RSD 2.4%	—	—	—	—	—	—
Dantrolene Sodium (Drug)	BiFE (ex situ on GCE)	DPAdSV	1.0 × 10 – 5.0 × 10 mol L ¹	LOD 5.0 × 10 ¹ mol L ¹	5.0×10 ¹	mol L ¹	5.0×10	-21.416	0.2	0.04
Cd(II)	SPE with Bi/Nafion film	DPV	Not specified	—	1.2	µg/L	1.2	0.182	0.2	0.04
Pb(II)	SPE with Bi/Nafion film	DPV	Not specified	—	0.8	µg/L	0.8	-0.223	0.2	0.04
Cd(II)	Paper-based carbon electrode with Bi film	LSV	2.5–10 µg/mL	—	1	µg/mL	1000	6.908	0.2	0.04
Pb(II)	Paper-based carbon electrode with Bi film	LSV	1–10 µg/mL	—	0.7	µg/mL	700	6.551	0.2	0.04

Cd(II)	Nanostructured conductive carbon tape with Bi	SWASV	0.1–0.2 µg/mL	—	0.1	µg/mL	100	4.605	0.2	0.04
Pb(II)	Nanostructured conductive carbon tape with Bi	SWASV	0.002–0.5 µg/mL	—	0.002	µg/mL	2	-6.215	0.2	0.04
Progesterone (Hormone)	Nanostructured Bi film electrode (nsBiFE)	AdCSV	0.1–0.7 µmol L ⁻¹	r ² = 0.99	—	µmol L ⁻¹	—	—	—	—

Table 3. Analytical Performance of Bismuth-Modified Carbon and Paper-Based Electrodes for Trace Heavy Metal Detection. This table compiles analytical data for heavy metal determination using bismuth-modified carbon, screen-printed, and paper-based electrodes. Key parameters include detection limits, linear range, and stripping techniques, illustrating their suitability as environmentally friendly alternatives to mercury electrodes.

Analyte	Electrode Substrate & Modification	Voltammetry Technique	Limit of Detection (LOD)	Linear Range	References
Cd(II)	Screen-printed electrode (SPE) with Bi/Nafion film	Differential pulse voltammetry (DPV)	1.2 µg L ⁻¹	Not specified	Dossi et al., 2016
Pb(II)	Screen-printed electrode (SPE) with Bi/Nafion film	Differential pulse voltammetry (DPV)	0.8 µg L ⁻¹	Not specified	Dossi et al., 2016
Cd(II)	Paper-based carbon electrode with bismuth film	Linear sweep voltammetry (LSV)	1 µg mL ⁻¹	2.5–10 µg mL ⁻¹	Sánchez-Calvo et al., 2020
Pb(II)	Paper-based carbon electrode with bismuth film	Linear sweep voltammetry (LSV)	0.7 µg mL ⁻¹	1–10 µg mL ⁻¹	Sánchez-Calvo et al., 2020; Guzsány et al 2011
Cd(II)	Nanostructured conductive carbon tape with bismuth	Square-wave anodic stripping voltammetry (SWASV)	0.1 µg mL ⁻¹	0.1–0.2 µg mL ⁻¹	Feng et al., 2013
Pb(II)	Nanostructured conductive carbon tape with bismuth	Square-wave anodic stripping voltammetry (SWASV)	0.002 µg mL ⁻¹	0.002–0.5 µg mL ⁻¹	Feng et al., 2013

demonstrating adequate sensitivity for regulatory compliance testing. In dairy matrices, solid-phase extraction combined with liquid chromatography has been used to quantify neonicotinoid residues in bovine milk, highlighting concerns regarding potential transfer into animal-derived food products (Seccia et al., 2008).

Advancements in analytical chemistry have further expanded detection capabilities through the use of liquid chromatography–mass spectrometry (LC–MS). This technique has enabled sensitive multiresidue determination of neonicotinoids in vegetables and fruits, improving selectivity and lowering detection limits compared with diode-array detection methods (Obana et al., 2003). Similarly, LC coupled with electrospray ionization mass spectrometry has been applied to detect nicotinoid insecticides in drinking water, addressing concerns related to environmental contamination and water quality monitoring (Seccia et al., 2005). These chromatographic approaches provide robust and validated methods; however, they often require complex instrumentation, extensive sample preparation, and centralized laboratory infrastructure.

Beyond chromatographic methods, alternative detection strategies have also been explored. Liquid chromatography with thermal lens spectrometric detection has been used for selected neonicotinoids, offering enhanced sensitivity under optimized laboratory conditions (Guzsvány et al., 2007). Earlier electrochemical approaches, such as pulsed reductive amperometric detection, were applied to determine imidacloprid and its metabolites in soil samples, demonstrating the feasibility of electroanalytical techniques for pesticide monitoring (de Erenchun et al., 1997). These studies illustrate the longstanding interest in developing more accessible and potentially field-deployable analytical methods.

Voltammetric techniques have gained attention as promising alternatives due to their relatively low cost, portability, and rapid response times. Early investigations demonstrated the voltammetric determination of imidacloprid and thiamethoxam using electrochemical methods, providing a foundation for pesticide analysis without reliance on high-end chromatographic systems (Guzsvány et al., 2005). Differential pulse polarography further enabled rapid determination of thiamethoxam in commercial formulations and real samples, highlighting the suitability of pulse-based electrochemical techniques for routine analysis (Guzsvány et al., 2006). Additionally,

carbon paste electrode systems have been successfully applied to the voltammetric determination of imidacloprid in selected matrices, reinforcing the adaptability of electrochemical platforms for neonicotinoid detection (Papp et al., 2009).

The growing regulatory scrutiny of neonicotinoids, combined with concerns about environmental persistence and potential ecological effects, underscores the need for analytical methods that are both sensitive and adaptable. While chromatographic techniques remain the gold standard for confirmatory analysis, electroanalytical methods offer complementary advantages, particularly in decentralized or resource-limited settings. Their compatibility with portable instrumentation makes them attractive for on-site monitoring of agricultural fields, water sources, and food products.

Overall, the analytical landscape for neonicotinoid detection reflects a balance between high-precision laboratory methods and emerging electrochemical alternatives. Foundational research on neonicotinoid chemistry and agricultural application (Jeschke & Nauen, 2008; Elbert et al., 2008) provides the context for understanding why accurate residue detection is essential. Subsequent advancements in chromatographic and electrochemical methodologies demonstrate the evolution of detection strategies in response to regulatory, environmental, and technological demands. Together, these studies highlight the importance of continuous methodological innovation to ensure reliable monitoring of neonicotinoid insecticides across diverse environmental and food matrices.

5. Limitations

This systematic review has several limitations. First, heterogeneity in electrode fabrication, modification techniques, and instrumental parameters across studies may have influenced the pooled outcomes. Second, while most studies focused on laboratory-controlled conditions, there is limited evidence from real environmental or complex biological matrices, which may affect analytical performance. Third, publication bias, though minimal, cannot be entirely excluded, particularly for smaller studies reporting highly positive results. Finally, variations in reporting analytical parameters, such as preconcentration steps or scan settings, may have affected direct comparability.

6. Conclusion

Pulling this literature together, a fairly consistent picture emerges: bismuth-based electrodes are not just a "safer mercury" but a genuinely competitive analytical platform in their own right, capable of reaching low- $\mu\text{g-per-liter}$ detection limits for classic heavy-metal targets while also handling pesticides, pharmaceuticals, and hormones with reasonable precision. That range is, arguably, the more interesting finding — it suggests bismuth's usefulness is not confined to the niche it was originally introduced to fill. That said, the evidence base remains comparatively small, methodologically varied, and — based on the nine studies eligible here — not yet large enough to support a fully confident pooled statistical estimate; larger, more standardized comparative studies, ideally reporting harmonized units and full variance data, would meaningfully strengthen future syntheses. For now, bismuth-based electrodes look like a well-supported, practical choice for portable and low-resource electroanalytical monitoring, with formal quantitative confirmation still catching up to the qualitative consensus.

References

- Baldrianová, L., Agrafiotou, P., Švancara, I., Vytras, K., & Sotiropoulos, S. (2008). The determination of cysteine at Bi-powder carbon paste electrodes by cathodic stripping voltammetry. *Electrochemistry Communications*, 10, 918–921. <https://doi.org/10.1016/j.elecom.2008.04.017>
- Baldrianová, L., Švancara, I., Vlcek, M., Economou, A., & Sotiropoulos, S. (2006). Effect of Bi(III) concentration on the stripping voltammetric response of in situ bismuth-coated carbon paste and gold electrodes. *Electrochimica Acta*, 52(2), 481–490. <https://doi.org/10.1016/j.electacta.2006.05.029>
- Borenstein, M., Hedges, L. V., Higgins, J. P. T., & Rothstein, H. R. (2009). *Introduction to meta-analysis*. Wiley. <https://doi.org/10.1002/9780470743386>
- Campestrini, I., De Braga, O. C., Vieira, I. C., & Spinelli, A. (2010). Application of bismuth-film electrode for cathodic electroanalytical determination of sulfadiazine. *Electrochimica Acta*, 55, 4970–4975. <https://doi.org/10.1016/j.electacta.2010.03.105>
- de Erenchun, N. R., de Balugera, Z. G., Goicolea, M. A., & Barrio, R. J. (1997). Determination of imidacloprid and its major metabolite in soils by liquid chromatography with pulsed reductive amperometric detection. *Analytica Chimica Acta*, 349, 199–206. [https://doi.org/10.1016/S0003-2670\(97\)00193-1](https://doi.org/10.1016/S0003-2670(97)00193-1)
- DerSimonian, R., & Laird, N. (1986). Meta-analysis in clinical trials. *Controlled Clinical Trials*, 7(3), 177–188. [https://doi.org/10.1016/0197-2456\(86\)90046-2](https://doi.org/10.1016/0197-2456(86)90046-2)
- Dossi, C., Binda, G., Monticelli, D., Pozzi, A., Recchia, S., & Spanu, D. (2020). Exploiting laser-ablation ICP-MS for the characterization of salt-derived bismuth films on screen-printed electrodes: A preliminary investigation. *Biosensors*, 10(9), 119. <https://doi.org/10.3390/bios10090119>
- Dossi, C., Monticelli, D., Pozzi, A., & Recchia, S. (2016). Exploiting chemistry to improve performance of screen-printed, bismuth film electrodes (SP-BiFE). *Biosensors*, 6(3), 38. <https://doi.org/10.3390/bios6030038>
- Economou, A. (2018). Screen-printed electrodes modified with "green" metals for electrochemical stripping analysis of toxic elements. *Sensors*, 18(4), 1032. <https://doi.org/10.3390/s18041032>
- Egger, M., Davey Smith, G., Schneider, M., & Minder, C. (1997). Bias in meta-analysis detected by a simple, graphical test. *BMJ*, 315(7109), 629–634. <https://doi.org/10.1136/bmj.315.7109.629>
- Elbert, A., Haas, M., Springer, B., Thielert, W., & Nauen, R. (2008). Applied aspects of neonicotinoid uses in crop protection. *Pest Management Science*, 64, 1099–1105. <https://doi.org/10.1002/ps.1616>
- Feng, Q. M., Zhang, Q., Shi, C. G., Xu, J. J., Bao, N., & Gu, H. Y. (2013). Using nanostructured conductive carbon tape modified with bismuth as the disposable working electrode for stripping analysis in paper-based analytical devices. *Talanta*, 115, 235–240. <https://doi.org/10.1016/j.talanta.2013.04.071>
- Guo, H., Chen, B., Luo, Y., Wang, R., Tian, Q., & Chang, Y. (2024). Effect of Bi(III)-to-metal ion concentration ratios on stripping voltammetric response of bismuth-film glassy carbon electrodes. *RSC Advances*, 14, 39361. <https://doi.org/10.1039/D4RA07034H>
- Guzsvány, V., Gaál, F., Bjelica, L., & Ökrész, S. N. (2005). Voltammetric determination of imidacloprid and thiamethoxam. *Journal of the Serbian Chemical Society*, 70, 735–743. <https://doi.org/10.2298/JSC0505735G>
- Guzsvány, V., Kádár, M., Gaál, F., Tóth, K., & Bjelica, L. (2006). Rapid differential pulse polarographic determination of thiamethoxam in commercial formulations and some real samples. *Microchimica Acta*, 154, 321–328. <https://doi.org/10.1007/s00604-006-0487-z>
- Guzsvány, V., Madžgalj, A., Trebše, P., Gaál, F., & Franko, M. (2007). Determination of selected neonicotinoid insecticides by liquid chromatography with thermal lens spectrometric detection. *Environmental Chemistry Letters*, 5, 203–208. <https://doi.org/10.1007/s10311-007-0102-5>
- Guzsvány, V., Papp, Z., Zbiljic, J., Vajdle, O., & Rodic, M. (2011). Bismuth modified carbon-based electrodes for the determination of selected neonicotinoid insecticides. *Molecules*, 16(6), 4451–4466. <https://doi.org/10.3390/molecules16064451>
- Higgins, J. P. T., Thomas, J., Chandler, J., Cumpston, M., Li, T., Page, M. J., & Welch, V. A. (2022). *Cochrane handbook for systematic reviews of interventions* (Version 6.3). Cochrane. <http://www.training.cochrane.org/handbook>
- Higgins, J. P. T., Thompson, S. G., Deeks, J. J., & Altman, D. G. (2003). Measuring inconsistency in meta-analyses. *BMJ*, 327(7414), 557–560. <https://doi.org/10.1136/bmj.327.7414.557>
- Hocevar, S., Švancara, I., Vytras, K., & Ogorevc, B. (2005). Novel electrode for electrochemical stripping analysis based on carbon paste modified with bismuth powder. *Electrochimica Acta*, 51(4), 706–710. <https://doi.org/10.1016/j.electacta.2005.05.023>

- Jeschke, P., & Nauen, R. (2008). Neonicotinoids-From zero to hero in insecticide chemistry. *Pest Management Science*, 64, 1084–1098. <https://doi.org/10.1002/ps.1631>
- Jeschke, P., Nauen, R., Schindler, M., & Elbert, A. (2011). Overview of the status and global strategy for neonicotinoids. *Journal of Agricultural and Food Chemistry*, 59, 2897–2908. <https://doi.org/10.1021/jf101303g>
- Kokkinos, C., Prodromidis, M., Economou, A., Petrou, P., & Kakabakos, S. (2015). Quantum dot-based electrochemical DNA biosensor using a screen-printed graphite surface with embedded bismuth precursor. *Electrochemistry Communications*, 60, 47–51. <https://doi.org/10.1016/j.elecom.2015.08.006>
- Królicka, A., & Korolczuk, M. (2024). Highly sensitive electrochemical method for thallium(I) determination using gold-based microelectrode array plated with bismuth film. *Sensors*, 24(4), 1206. <https://doi.org/10.3390/s24041206>
- Mandic, A., Lazic, S., Ökrész, S. N., & Gaál, F. (2005). Determination of the insecticide imidacloprid in potato (*Solanum tuberosum* L.) and onion (*Allium cepa*) by high-performance liquid chromatography with diode-array detection. *Journal of Analytical Chemistry*, 60, 1134–1138. <https://doi.org/10.1007/s10809-005-0256-x>
- March, G., Nguyen, T. D., & Piro, B. (2015). Modified electrodes used for electrochemical detection of metal ions in environmental analysis. *Biosensors*, 5(2), 241–275. <https://doi.org/10.3390/bios5020241>
- Obana, H., Okihashi, M., Akutsu, K., Kitagawa, Y., & Hori, S. (2002). Determination of acetamiprid, imidacloprid, and nitenpyram residues in vegetables and fruits by high-performance liquid chromatography with diode-array detection. *Journal of Agricultural and Food Chemistry*, 50, 4464–4467. <https://doi.org/10.1021/jf025539q>
- Obana, H., Okihashi, M., Akutsu, K., Kitagawa, Y., & Hori, S. (2003). Determination of neonicotinoid pesticide residues in vegetables and fruits with solid-phase extraction and liquid chromatography-mass spectrometry. *Journal of Agricultural and Food Chemistry*, 51, 2501–2505. <https://doi.org/10.1021/jf0261102>
- Page, M. J., McKenzie, J. E., Bossuyt, P. M., Boutron, I., Hoffmann, T. C., Mulrow, C. D., et al. (2021). The PRISMA 2020 statement: An updated guideline for reporting systematic reviews. *BMJ*, 372, n71. <https://doi.org/10.1136/bmj.n71>
- Papp, Z., Švancara, I., Guzvány, V., Vytras, K., & Gaál, F. (2009). Voltammetric determination of imidacloprid insecticide in selected samples using a carbon paste electrode. *Microchimica Acta*, 166, 169–175. <https://doi.org/10.1007/s00604-009-0181-z>
- Sánchez-Calvo, A., Blanco-López, M. C., & Costa-García, A. (2020). Paper-based working electrodes coated with mercury or bismuth films for heavy metals determination. *Biosensors*, 10(5), 52. <https://doi.org/10.3390/bios10050052>
- Seccia, S., Fidente, P., Barbini, D. A., & Moricca, P. (2005). Multiresidue determination of nicotinoid insecticide residues in drinking water by liquid chromatography with electrospray ionization mass spectrometry. *Analytica Chimica Acta*, 553, 21–26. <https://doi.org/10.1016/j.aca.2005.08.006>
- Seccia, S., Fidente, P., Montesano, D., & Morrica, P. (2008). Determination of neonicotinoid insecticide residues in bovine milk samples by solid-phase extraction clean-up and liquid chromatography with diode-array detection. *Journal of Chromatography A*, 1214, 115–120. <https://doi.org/10.1016/j.chroma.2008.10.088>
- Šelešovská, R., Martinková, P., Štěpánková, M., Navrátil, T., & Chýlková, J. (2017). Comparison study of voltammetric behavior of muscle relaxant Dantrolene sodium on silver solid amalgam and bismuth film electrodes. *Journal of Analytical Methods in Chemistry*, 2017, 3627428. <https://doi.org/10.1155/2017/3627428>
- Švancara, I., Baldrianová, L., Váček, M., Metelka, R., & Vytras, K. (2005). A role of the plating regime in the deposition of bismuth films onto a carbon paste electrode: Microscopic study. *Electroanalysis*, 17(2–3), 120–126. <https://doi.org/10.1002/elan.200403061>
- Švancara, I., Prior, C., Hocevar, S. B., & Wang, J. (2010). A decade with bismuth-based electrodes in electroanalysis. *Electroanalysis*, 22(13), 1405–1420. <https://doi.org/10.1002/elan.200970017>
- Wang, J., Lu, J., Hocevar, S. B., Farias, P. A. M., & Ogorevc, B. (2000). Bismuth-coated carbon electrodes for anodic stripping voltammetry. *Analytical Chemistry*, 72(14), 3218–3222. <https://doi.org/10.1021/ac000108x>
- Zidaric, T., Jovanovski, V., Menart, E., Zorko, M., Kolar, M., Veber, M., & Hocevar, S. B. (2018). Nanostructured bismuth film electrode for adsorptive cathodic stripping voltammetric detection of progesterone. *Sensors*, 18(12), 4233. <https://doi.org/10.3390/s18124233>