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Electrochemical Detection of Selected Antifungal Agents

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Abstract : *Electrochemical detection provides an analytical approach for determining antifungal agents in pharmaceutical preparations, biological samples, and aqueous environments. Its effectiveness depends on the relationship between molecular structure, electrode composition, solution chemistry, and measurement conditions. This review examines selected studies involving ketoconazole, fluconazole, itraconazole, posaconazole, and voriconazole, with particular attention to carbon electrodes, nanocomposite modifications, and voltammetric methods. Published evidence demonstrates that the same antifungal compound can exhibit substantially different responses across electrode systems. Four ketoconazole sensors are compared quantitatively using reported detection limits, while other antifungal agents illustrate the importance of adsorption, solvent selection, and reaction mechanisms. The comparison identifies promising analytical performance but also highlights limitations associated with comparing independently optimized methods. A proposed validation framework addresses calibration, selectivity, electrode reproducibility, sample preparation, and agreement with reference measurements. Future research should prioritize reliable performance in realistic samples, transparent reporting, and practical manufacturing. Electrochemical sensors offer considerable potential, provided that improvements in detection capability are accompanied by convincing evidence of analytical accuracy and application suitability.*

Key Words: Electrochemical Detection of Selected Antifungal Agents

I. INTRODUCTION

The determination of antifungal agents is an important analytical task because pharmaceutical formulations and complex sample matrices require reliable identification and quantification of their chemical constituents. A suitable analytical method must distinguish the target compound from accompanying substances while producing reproducible concentration estimates. Electrochemical research addresses this requirement through measurements of electrical responses generated at electrode interfaces.

The selected literature includes applications involving pharmaceutical formulations, biological fluids, and water samples. For example, a ketoconazole sensor incorporating fluorinated carbon quantum dots and nickel oxide nanoparticles was evaluated in pharmaceutical products and tap water. Another platform combining carbon black, chitosan, and gold nanoparticles was applied to pharmaceutical and biological samples. These studies demonstrate the breadth of investigated applications without establishing that every sensor is suitable for every matrix (Silva et al., 2021; dos Santos et al., 2025).

Antifungal compounds cannot be treated as electrochemically interchangeable. Their functional groups, adsorption behaviour, and interactions with the supporting electrolyte influence the signals available for measurement. Fluconazole illustrates this distinction particularly clearly: oxidation was reported using carbon electrodes, whereas a separate investigation found no activity under its dropping-mercury polarographic conditions. The difference reflects the measurement systems rather than a contradiction about the compound itself (Gil et al., 2011; Knoth et al., 2012).

This paper reviews representative detection strategies and critically compares their analytical implications. Its central question is how electrode design and experimental conditions influence dependable antifungal determination. The

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contribution is a structured interpretation of selected evidence, accompanied by a quantitative graph, a comparison table, and a proposed framework for future experimental validation.

II. REVIEW METHODOLOGY

A focused narrative review was conducted using targeted web searches and examination of primary research records from publishers, PubMed, and an institutional repository. Search combinations included antifungal names with electrochemical detection, voltammetry, modified electrode, and detection limit. Studies were selected when accessible records identified the analyte, electrode platform, measurement approach, or quantitative analytical performance.

The review is selective and does not claim systematic coverage or a pooled statistical analysis. Where full articles were unavailable, interpretation was restricted to information in accessible abstracts and bibliographic records. Missing validation details were not assumed to be satisfactory or absent.

Four ketoconazole studies were chosen for graphical comparison because each explicitly reported a detection limit. Concentrations were converted to nanomoles per litre using the relationship that one micromole per litre equals one thousand nanomoles per litre. Reported calibration ranges were retained in micromoles per litre. No experimental currents, replicate measurements, uncertainty intervals, or additional concentration values were generated.

The remaining studies support discussion of differences between antifungal compounds and detection principles. Proposed experimental procedures are presented separately from published findings.

III. ELECTROCHEMICAL PRINCIPLES AND MEASUREMENT SELECTION

Electrochemical measurements connect an applied or measured potential with processes occurring at an electrode–solution interface. In voltammetric analysis, the potential changes according to a selected waveform while current is recorded. An analytically useful response requires a reproducible relationship between the measured signal and analyte concentration.

Cyclic voltammetry is particularly useful during initial method development because repeated forward and reverse scans reveal changes in electrochemical behaviour. In their investigation of itraconazole, posaconazole, and ketoconazole, Knoth and colleagues observed irreversible oxidation together with additional reduction and oxidation features. They proposed molecular interpretations for these processes under their specific experimental conditions. Such mechanistic observations should be distinguished from independent confirmation of reaction products (Knoth et al., 2015).

Pulse methods provide alternative ways to measure concentration-dependent signals. Differential pulse voltammetry was used for the cerium metal–organic framework ketoconazole sensor, while square-wave voltammetry supported quantification with the fluorinated carbon-dot/nickel-oxide platform. Their reported analytical performance belongs to the complete experimental method, including electrode fabrication, electrolyte composition, and waveform settings (Tajik et al., 2023; dos Santos et al., 2025).

Potentiometry represents a different analytical route. Hussein and colleagues investigated fluconazole-selective polymeric membrane electrodes incorporating cyclodextrin-related recognition chemistry and magnetic iron oxide particles. Applications included spiked plasma and milk. Because potentiometric responses and detection-limit estimation differ from voltammetric measurements, their numerical performance should not be combined uncritically in a single ranking (Hussein et al., 2015).

For future method selection, the decisive consideration should be the intended measurement problem. A concentrated formulation assay and a trace-level biological analysis may require different calibration ranges, sample treatments, and selectivity controls even when they concern the same drug.

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IV. PUBLISHED FINDINGS FOR SELECTED ANTIFUNGAL AGENTS

4.1 Ketoconazole

Ketoconazole provides the strongest quantitative comparison within the selected evidence. Saleh and colleagues developed a gold-nanoparticle-modified carbon paste electrode with a reported detection limit of 0.1 µmol/L and a calibration range of 1–80 µmol/L. This study demonstrates an approach based on modifying a conventional carbon paste surface (Saleh et al., 2018).

Tajik and colleagues investigated a carbon paste electrode containing a cerium-based metal–organic framework and ionic liquid. Their reported detection limit was 0.04 µmol/L, with a linear concentration interval extending from 0.1 to 110 µmol/L. The study combined material characterization with electrochemical investigation, linking electrode preparation to analytical performance (Tajik et al., 2023).

Silva and colleagues reported a lower detection limit of 4.4 nmol/L using carbon black and chitosan-stabilized gold nanoparticles on glassy carbon. Its calibration interval was 0.10–2.9 µmol/L. The comparatively narrow range illustrates why detection capability and working concentration range should be evaluated separately (Silva et al., 2021).

The fluorinated carbon-dot/nickel-oxide sensor reported by dos Santos and colleagues achieved a detection limit of 7.12 nmol/L. Its calibration interval extended from 0.037 to 11.13 µmol/L, and reported recoveries ranged from 88.8% to 103.6%. These findings provide application evidence under the tested conditions, rather than universal validation across water or pharmaceutical matrices (dos Santos et al., 2025).

4.2 Fluconazole

Gil and colleagues demonstrated that fluconazole oxidation depended strongly on electrode material. Reactant adsorption occurred at platinum, while oxidation-product adsorption was observed on glassy carbon. Using carbon paste in phosphate buffer at pH 8, the study reported a detection limit of 6.3 µg/mL and a linear range of 48–250 µg/mL (Gil et al., 2011).

The analytical implication is that surface history deserves explicit control. If an electrode accumulates reaction products, consecutive measurements may reflect both concentration and previous exposure. A proposed fluconazole protocol should therefore compare fresh surfaces, repeated measurements, and defined regeneration procedures before adopting routine calibration.

4.3 Itraconazole and posaconazole

The glassy-carbon investigation by Knoth and colleagues examined itraconazole and posaconazole alongside ketoconazole in a phosphate-buffer/acetonitrile mixture. The authors associated higher-potential oxidation with the piperazine component of these structures. Their results support examining individual reaction features rather than assuming that membership in the azole class determines one common analytical response (Knoth et al., 2015).

For future comparative work, solvent composition should be recorded and held constant during calibration. Any procedure that changes solvent content when standards are added should test whether the change itself influences current. Otherwise, a concentration-dependent response may include an uncontrolled contribution from the measurement medium.

4.4 Voriconazole

Knoth, Petry, and Gärtner investigated voriconazole by differential pulse polarography using a dropping mercury electrode. A reduction response was reported under alkaline conditions, whereas ketoconazole and itraconazole showed responses under different pH conditions. Fluconazole did not exhibit electrochemical activity in that investigation (Knoth et al., 2012).

These findings reinforce the need for compound-specific optimization. Developing a shared platform for several antifungal agents should begin with separate characterization of each analyte before testing mixtures or proposing simultaneous quantification.

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V. COMPARISON OF REPORTED ANALYTICAL PERFORMANCE

Table 1. Published electrochemical methods for antifungal determination

Antifungal	Electrode platform	Linear range	Detection limit	Source
Ketoconazole	AuNPs/CPE	1–80 µmol/L	100 nmol/L	Saleh et al. (2018)
Ketoconazole	Ce-BTC and IL/CPE	0.1–110 µmol/L	40 nmol/L	Tajik et al. (2023)
Ketoconazole	CB–CTS–AuNPs/GCE	0.10–2.9 µmol/L	4.4 nmol/L	Silva et al. (2021)
Ketoconazole	F-Cdots–NiO/GCE	0.037–11.13 µmol/L	7.12 nmol/L	dos Santos et al. (2025)
Fluconazole	Carbon paste	48–250 µg/mL	6.3 µg/mL	Gil et al. (2011)

The table compares independently developed methods using their reported calibration intervals and detection limits. Fluconazole retains its original mass-concentration units and is excluded from the graph. This avoids mixing unlike units and keeps the graphical comparison focused on one analyte.

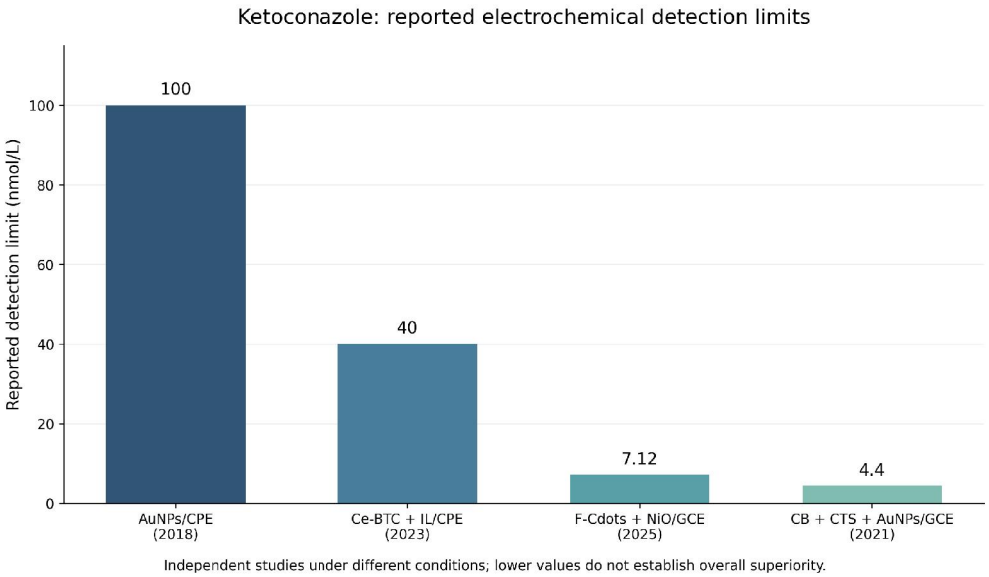


Figure 1. Reported ketoconazole detection limits in independent studies. Sources: Saleh et al. (2018), Tajik et al. (2023), dos Santos et al. (2025), and Silva et al. (2021). Lower values do not establish overall superiority.

Abbreviations: AuNPs, gold nanoparticles; CPE, carbon paste electrode; IL, ionic liquid; F-Cdots, fluorinated carbon quantum dots; GCE, glassy carbon electrode; CB, carbon black; CTS, chitosan.

The graph shows approximately a twenty-three-fold numerical difference between the largest and smallest reported detection limits. This is a calculation from published values, not evidence of a twenty-three-fold improvement under matched conditions. Electrode area, signal processing, blank variability, and sample preparation may differ between studies.

The table also reveals a practical trade-off: the method with the smallest detection limit does not have the widest calibration range. A laboratory measuring comparatively concentrated samples could value a broad working interval and straightforward dilution more than the lowest attainable detection threshold.

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VI. PROPOSED EXPERIMENTAL AND VALIDATION FRAMEWORK

The following framework is proposed for future research and was not performed for this review. Its purpose is to connect sensor development with a clearly defined analytical application.

First, investigators should specify the target compound, sample type, expected concentration interval, and intended decision. These choices should guide electrode selection. A sensor intended for formulation analysis should be evaluated using representative excipients and extraction conditions, while a biological application requires attention to sample variability and analyte recovery.

Second, electrode development should include an unmodified control and controls containing individual modifier components. Comparing only the final composite with a bare electrode cannot establish which component contributes to performance. Modifier loading, preparation time, drying conditions, and storage should be documented sufficiently for another laboratory to reproduce the surface.

Third, electrochemical screening should investigate solution pH, solvent fraction, potential window, and repeated-scan behaviour. Optimization should consider signal stability and blank response alongside peak height. The largest peak should not automatically be accepted as the best operating condition if it also produces unstable background current or rapid surface deterioration.

Calibration should use independently prepared standards spanning the intended working interval. Replicate measurements at several concentrations should help reveal changing variability across the range. Residual patterns should be examined because a high correlation coefficient alone cannot demonstrate that a linear model adequately describes the data.

Detection and quantification limits should be calculated using a stated approach and then checked experimentally near the proposed lower boundary. If a calculation uses calibration slope and response variability, the origin of that variability must be identified. Blank variation, regression residual variation, and repeated low-level measurements are not interchangeable without justification.

Selectivity experiments should include substances relevant to the actual sample. For pharmaceutical products, this means representative excipients and plausible degradation products. For biological samples, it means endogenous constituents and relevant co-administered compounds. Testing substances individually should be supplemented with mixtures where combined interference is plausible.

Repeatability should be separated from fabrication reproducibility. Repeated measurements using one electrode assess a different source of variation from measurements across independently prepared electrodes. Testing different preparation batches and measurement days would provide stronger evidence of method reliability.

Sample preparation should be evaluated as part of the complete procedure. Recovery experiments should distinguish losses during extraction from effects introduced during electrochemical measurement. Spiking before and after preparation can help identify these contributions, provided that the experimental design accounts for the original analyte content.

Finally, a suitably validated reference method should be used for agreement testing. Comparisons should examine concentration-dependent differences and uncertainty, rather than relying exclusively on correlation. The resulting evidence would support a defensible statement about the sensor's intended analytical use.

VII. RESEARCH GAPS AND FUTURE DIRECTIONS

The reviewed evidence motivates several research priorities. These are analytical recommendations arising from the comparison, rather than claims that every published study omitted the relevant experiments.

The first priority is standardized comparison. Independent sensors should be tested with common samples, equivalent concentration ranges, and transparent detection-limit calculations. Such a design would help distinguish improvements caused by electrode chemistry from those caused by different experimental settings.

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The second priority is stronger matrix validation. Successful recovery from a limited set of spiked samples should lead to broader testing across independently sourced materials. Where naturally occurring analyte is measurable, agreement with a reference method would provide more persuasive application evidence than spiking alone.

The third priority is realistic selectivity. Structurally related antifungal compounds may require deliberate testing because similar electrochemical features could complicate identification. Mixture experiments should examine concentration ratios as well as peak positions. A visually distinct peak in a simple solution does not establish reliable quantification in a changing mixture.

The fourth priority concerns manufacturing and usability. Future studies should report the time, material requirements, and variability involved in electrode preparation. A promising laboratory surface must retain its performance when prepared repeatedly, stored, transported, and used by different operators.

The fifth priority is transparent data reporting. Raw voltammograms, blank measurements, calibration observations, and fabrication details should accompany headline performance values where possible. Accessible data would allow others to assess baseline treatment, model selection, and uncertainty.

Environmental evaluation should also examine the complete analytical workflow. Proposed reductions in solvent consumption or instrument requirements should be balanced against modifier synthesis, cleaning procedures, electrode disposal, and sample pretreatment. This broader accounting would make claims of practical sustainability more meaningful.

A useful extension would be a blinded comparison in which the analyst receives samples without knowing their assigned concentrations. Calibration standards and assessment samples should come from separate preparations, reducing the chance that a common preparation error makes agreement appear better than it is. The study could include low, intermediate, and high concentrations alongside samples containing no target compound. Results should be interpreted against acceptance criteria established before measurement, with failed analyses retained in the report rather than excluded without explanation.

Instrument transfer should also be investigated before a portable application is claimed. A method optimized on a laboratory potentiostat could be repeated on the intended compact instrument using the same electrodes and sample preparations. Differences in potential control, current measurement, or available waveform settings should be documented. The relevant outcome is agreement in estimated concentration across the intended range, together with a realistic account of analysis time and operator effort.

Longer storage studies would further clarify whether calibration remains usable after electrode preparation. Measurements at planned intervals should examine both signal retention and changes in background response. Packaging conditions, temperature, and exposure to moisture should be recorded. These experiments would help define a supported storage period and identify when recalibration or electrode replacement is required for dependable operation in laboratory practice and field settings.

VIII. CONCLUSION

Electrochemical detection offers several approaches for determining selected antifungal agents, but reliable performance depends on the complete measurement system. The reviewed studies demonstrate compound-specific responses and substantial differences among electrode platforms. Ketoconazole sensors provide quantitative examples of low reported detection limits, while fluconazole and other azoles illustrate the importance of surface interactions and experimental conditions.

The comparison supports evaluating detection capability alongside calibration range, selectivity, reproducibility, and matrix performance. Future investigations should prioritize matched comparisons and application-focused validation. Progress toward dependable analytical use will require clear evidence that sensor performance survives realistic sample preparation, electrode fabrication variability, and independent verification.

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