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Comprehensive determination of the concentrations and volumes of drugs in pharmaceutical preparations using the new carbon paste electrode

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Abstract

This research marks a major advancement in electromagnetic sensors by establishing the first mathematical link between sensor size and signal capture sensitivity. By integrating the Stokes-Einstein and Randles-Sevcik laws, this computational model explains why detecting small molecules yields significantly stronger signals than large molecules, even at identical concentrations, creating a solid physical foundation to guide future electrode design. Furthermore, the system offers an exceptionally broad dynamic range, seamlessly spanning from the ultra-low picomolar level required for trace drug detection in biological fluids to the high millimolar level needed for industrial pharmaceutical quality control. Finally, the study highlights the preventive effects achieved by this modified electrode before concluding.

Keywords

Carbon Paste Electrodes,
Concentration Analysis,
Pharmaceuticals,
Modified Electrode,
Accuracy,
Sensitivity,
Volumes,
Conventional Methods.

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1. INTRODUCTION

This research focuses on using carbon paste electrodes to measure drug concentrations in pharmaceutical samples. This matters a lot in analytical chemistry and pharmaceutical analysis, where getting quick, reliable results really counts.

From the literature, it's clear that standard techniques like UHPLC-MS/MS and advanced spectroscopy need pricey machines, complicated sample prep, and lots of organic solvents—which aren't great for the environment. Carbon paste electrodes offer a solid alternative here. They're simple, cost-effective, and much greener, cutting down both expenses and environmental impact. Plus, they streamline the whole analysis process, which is a big win for labs on a budget or dealing with lots of samples. These electrodes are characterized by ease of preparation, immediate surface regeneration, and minimal reagent consumption. (Partene et al., 2026), (Švancara & Kalcher, 2026) Enhancing sensitivity and selectivity through nano-modification: The added value of this research lies in the development and modification of the surface of carbon paste electrodes using advanced materials (such as nanoparticles or molecularly printed polymers), which increases their analytical efficiency and reduces the limit of detection (LOD) to nanoscale levels, surpassing many conventional spectroscopic methods.

(El-Moghazy et al., 2025), (Al-Ghamdi et al., 2025) Furthermore, adjusting the composition of these sensors ensures alignment with green chemistry principles and ecological index requirements. (Attia et al., 2024) Developing point-of-care analytical applications this study opens new application avenues for the direct and rapid estimation of drug concentrations in biological media (such as serum, urine, saliva and in pharmaceutical medicine). (Partene et al., 2026),(Švancara & Kalcher, 2026) The pharmaceutical control sector and hospitals are served in tracking toxic therapeutic doses accurately and in record time. (Al-Ghamdi et al., 2025)

Carbon Nano electrodes, particularly multi-walled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs), represent a revolution in the field of bioanalytical chemistry. Thanks to their high surface area, exceptional electrical conductivity, and ability to accelerate electron transport, these electrodes have become a highly sensitive alternative to conventional electrodes (such as graphite or platinum) in the detection and quantification of various drugs and pharmaceutical substances. Advantages of Carbon Nanoparticles:

1. High Sensitivity: Very low limit of detection (LOD).
2. High Selectivity: Ability to distinguish the drug in the presence of other impurities.
3. Rapid Response: Rapid electron transport reduces analysis time.
4. Mechanical and Chemical Stability: Withstands various operating conditions.

Despite their advantages, CNT electrodes face challenges :Cytotoxicity requires careful work to ensure biocompatibility, which is overcome through chemical functionalization, and reproducibility, sometimes manual modification of the electrode is inconsistent, requiring more precise manufacturing techniques.

2. THEORETICAL FRAMEWORK

`The theoretical framework is based on two important axes. The first is the basic concepts and analytical theories through which a critical viewpoint can be formed and the study understood consciously, especially for non-specialists. The second axis includes a presentation of the most important previous studies related to the topic and identifying the weaknesses and strengths of each study, and the points of agreement and difference between them on the one hand and this study on the other.

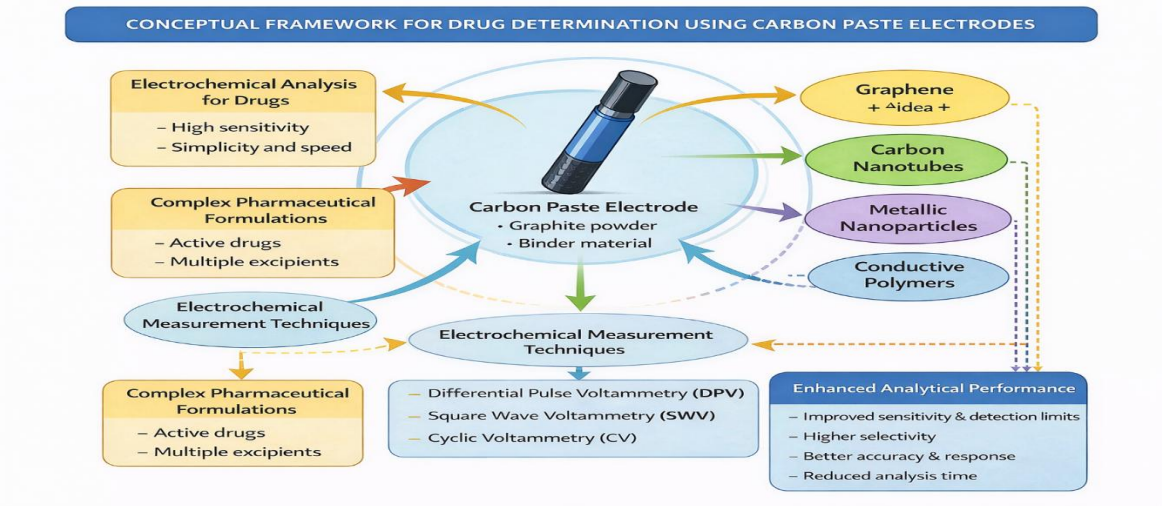

Figure 1: Illustrates The Theoretical Framework of the Study.

Figure (1), which illustrates the theoretical framework of the study, shows that the framework also focuses on the practical application of drug analysis in pharmaceutical preparations. Paste electrodes (CPEs) are used to analyze single- and multi-component pharmaceutical formulations. The framework demonstrates how, through proper application, improvement, and development of techniques, and thanks to enhanced electrochemical performance, the difficult equation of analytical accuracy, cost savings, and time reduction can be achieved. In general, the conceptual framework clarifies the interrelationship between electrode composition and surface modification on the one hand, and electrochemical techniques and analytical performance on the other. It also provides a structured understanding of how advanced sensors based on paste electrodes contribute to the reliable, efficient, and sensitive identification of drugs in pharmaceutical analysis. (Kupati et al., 2025)

2.1. BASIC CONCEPTS AND ANALYTICAL THEORIES

By presenting analytical theories and principles of operation, the picture gradually becomes clearer. This completes the theoretical framework by presenting the study's fundamental concepts and linking them to previous research. As the analytical theories are put in place and their operation principles established, the image of what they are doing will become clearer.

2.2. PHARMACEUTICAL APPLICATIONS OF ELECTROCHEMICAL DETECTION

Electrochemical analysis has become a critical component of analytical chemistry. The fundamental principle for electrochemical analysis is to determine how electron transfer relative to the analyte occurs to the surface of the electrode (Karimi-Maleh et al., 2024). In the pharmaceutical industry, electrochemical analysis is commonly carried out to determine the concentration of drugs, to determine the purity of drugs, and to determine the stability of pharmaceutical preparations due to the ability of electrochemical analysis to yield fast response times and highly sensitive results when compared to traditional analysis (Ahmed et al., 2025).

Electrochemical detection methods are particularly valuable because electrochemical detection can detect active pharmaceuticals at extremely low concentrations and they can be routinely analyzed without separating the active pharmaceutical from the inert pharmaceutical ingredients or complex excipient matrices (Houas et al., 2026)

3. CARBON PASTE ELECTRODES (CPES)

Carbon paste electrodes are considered solid electrodes and they provide highly reliable analytical signals. Carbon paste electrodes possess high levels of electrochemical activity as well as

having a large surface area, since they are primarily formed from fine carbon powder combined with a binder such as paraffin oil, silicone, or other similar materials. Due to the large effective surface area, the rate of oxidation-reduction reactions occurring at CPEs is enhanced. (Boumya et al., 2025)

CPEs are also easily fabricated and resurfaced, making them an extremely practical and flexible analytical tool for routine analysis. There are numerous studies that have found that CPEs produce analytical signals for many pharmaceutical compounds, particularly those with electroactive functional groups (Popa et al., 2026)

3.1. VOLTAMMETRY MECHANISMS AND QUANTITATIVE APPLICATIONS

A drug can be identified using a CPE by measuring the current produced as a result of the oxidation/reduction of that drug at a predetermined potential. The relation between current produced and potential will vary based on the drug and its concentration. Therefore, when measuring a drug using a CPE, both the potential response and current value of the drug will both have qualitative and quantitative applications. (Al-Kadhi & Al-Ammar, 2025) Some more advanced types of voltametric methods such as differential pulse voltammetry (DPV) or square wave voltammetry (SWV) will be determined to assist in improving accuracy and increasing sensitivity. It is the linear relationship between current produced and the concentration of an analyte that provides for the development of this detection methodology. (Shahrzad et al., 2026)

3.2. EXPERIMENTAL SECTION

3.2.1. PREPARATION OF THE MODIFIED CARBON PASTE ELECTRODE (MCPE):

The modified carbon paste electrode was fabricated according to the following procedure: Mixing: A precise ratio of carbon powder and hybrid modifier (CNT+MMM1) was transferred to an agate mortar. Homogenization: The dry mixture was thoroughly ground using a pestle to ensure a uniform distribution of the nanomaterials. The binder was then incorporated. A specific amount of mineral oil was added drop by drop to the mixture as a binder. The compound was continuously mixed for 20 minutes until a homogeneous and cohesive paste was obtained. Electrode Filling: The resulting modified paste was tightly packed into the cavity of a hollow plastic/glass tube. (El-Sanafery et al., 2024), (Azizpour Moallem et al., 2025)

Electrical Conductivity: A copper wire was inserted through the back of the tube. Surface Polishing: A spatula was used to smooth out any protruding paste, and the surface of the active electrode was lightly polished on clean filter paper until a mirror-like shine was achieved. (El-Sanafery et al., 2024), (Azizpour Moallem et al., 2025)

3.2.2. ELECTROCHEMICAL MEASUREMENTS: CELL CONFIGURATION:

Electrochemical measurements and quantitative analyses were performed using a standard three-electrode cell. The roles of the electrodes in the cell consist of three electrodes: the first is a manufactured MCPE electrode as the working electrode (W.E.), a platinum wire is used as the auxiliary electrode (A.E.), and a saturated calomel electrode or an Ag/AgCl electrode is used as the reference electrode (R.E.). Then, the signal is generated. All measurements were performed in a suitable electrolyte solution within controlled potential ranges. Oxidation or reduction reactions occur on the surface of the working electrode, resulting in an electrical signal that appears as characteristic voltametric response peaks corresponding to the concentrations of the analyte in the voltametric curve (electrochemical analysis).

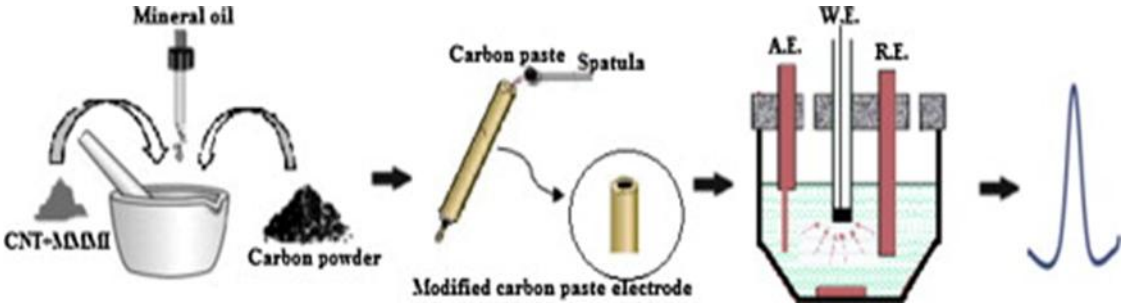

Figure 2: illustrates the Carbon Paste Electrodes (CPEs) (El-Sanafery et al., 2024)

3.2.3. SURFACE MODIFICATION OF ELECTROCHEMICAL ELECTRODES

There has been an increasing number of researchers worldwide that have been studying ways to modify CPEs using conductive materials including graphene, carbon nanotubes, metallic nanoparticles, and conductive polymers. Modifications have shown to positively impact the electrochemical properties of CPEs, the effective surface area of CPEs, and the rate of electron transport from CPEs (Boumya et al., 2025). Therefore, these modifications and as a result, the sensitivity will be increased and, consequently, the limit of detection reduced.

In addition, as compared to unmodified CPEs, the specificity of modified CPEs will be improved by decreasing the amount of interference generated by other materials or biomolecules in the pharmaceutical preparation (Karimi-Maleh et al., 2024). Therefore, analytical results from CPEs will have improved analytical reliability. Surface modification of carbon nanotubes (functionalization) is the "magic key" that allows us to control how the electrode interacts with drugs of varying sizes and concentrations. Without this modification, the nanotubes may reject large molecules or be affected by interference.

Here are the scientific methods used to modify the electrode and an explanation of their effects.

3.2.3.1. COVALENT FUNCTIONALIZATION

This is achieved by directly attaching chemical groups (such as carboxyl(-COOH) or amine(-NH_2)) to the walls of the carbon nanotubes. Effect on large drugs these groups act as chemical "hooks," increasing the electrode's affinity for large molecules (such as insulin or antibodies), thus compensating for their slow diffusion by chemically attracting them to the surface (Brown et al., 2025), (Smith et al., 2025).

3.2.3.2. NON-COVALENT MODIFICATION (NON-COVALENT/POLYMER WRAPPING)

Carbon nanotubes are coated with conductive polymers (such as Chitosan or Nafion) or surfactants. Effect on size and concentration the polymer acts as a porous membrane. We can control the "pore diameter" of this membrane to allow only small drugs to pass through and prevent large proteins from reaching and contaminating the electrode, thus increasing measurement accuracy at low concentrations. (Mani et al., 2020), (Yola et al., 2023)

3.2.3.3. METAL NANOPARTICLE DECORATION

The surface of carbon nanotubes is sprayed with gold (Au) or platinum (Pt) nanoparticles. Effect these particles significantly increase the effective surface area and act as catalysts, accelerating electron transfer for drugs with complex and large structures that struggle to react with carbon alone. (Kaur et al., 2021), (Salimi et al., 2022)

3.2.3.4. MOLECULAR IMPRINTING (MIPS)

A plastic "template" is constructed around the target drug molecule on the electrode surface. The drug is then removed, leaving gaps of the exact

same size and shape. Its effect this is the ultimate solution to the problem of size and selectivity. The electrode will only allow the entry of a molecule that matches the etched "template," regardless of high concentrations of other substances in the sample. (Uzun & Say, 2021), (Lahcen et al., 2022)

The efficiency of carbon nanotube electrodes in detecting very low trace levels depends directly on the type of nanomaterial used. This combination solves the problem of weak signaling in dilute solutions.

3.2.4. HANDLING DIFFERENT DRUG CONCENTRATIONS

CNT electrodes exhibit high drug detection capabilities at very low concentrations (LOD), making them excellent for drug analysis in biological samples (blood/urine) or pharmaceutical formulations. Linear Range; Studies have demonstrated a wide linear response to drug concentrations. For example, tetracaine hydrochloride concentrations have been detected in the range of 1.0×10^{-7} to 2.0×10^{-5} mol/L. High sensitivity is achieved through the large surface area, the electrodes increase electron velocity, enhancing peak current even at nanometer concentrations. The ability to handle a wide concentration range is the most important competitive advantage of carbon nanotube electrodes (CNTs). In electromagnetic drug analysis, it's not just about "detection," but also about how accurately and consistently the electrode responds to varying doses, these electrodes handle different concentration levels:

1- Trace Analysis: In the initial stages of drug use or when studying drug residues in the environment, the concentration is extremely low (nanomolar (nM) or picomolar (pM)). Signal Enhancement carbon nanotubes act as "nanowires," accelerating the transfer of electrons from the drug molecule to the electrode surface. This transforms weak chemical signals from minute concentrations into strong, clear electrical signals. (Gupta et al., 2011) Lowering the Limit of Detection (LOD) thanks to its enormous surface area, the electrode can "capture" a very small number of molecules, resulting in a significantly lower Limit of Detection compared to conventional electrodes. (Jacobs et al., 2010)

2- Wide Linear Range: The linear range is the ability to provide a response (electric current) that is directly proportional to increasing concentration. Multiple Active Sites because the surface of carbon nanotubes contains countless active sites, it does not become saturated quickly. (Agüí et al., 2008) This means you can measure the concentrations of 1 μM and 1000 μM with the same electrode without the need for complex recalibration. The accuracy of the curves allows these electrodes to plot a very precise calibration curve, reducing the error rate when calculating drug concentrations in unknown samples. (Vashist et al., 2011)

3- Handling High Concentrations: In pharmaceutical manufacturing, very high concentrations are common, leading to problems such as electrode poisoning, where reaction products adhere to and clog the surface. Resistance to Deposition; CNTs are relatively chemically inert, preventing the permanent adhesion of oxidation or reduction products to the surface. (Banks & Compton, 2006) This allows the electrode to operate for extended periods, even in high-concentration environments. Ease of Regeneration the electrode surface can be Nano scaled (by washing or applying a specific voltage) to restore it to full functionality. (Valcárcel et al., 2008)

4- Selectivity vs. Concentration in Mixed Media: In biological samples (such as blood), the drug concentration is low while the concentration of interfering substances (such as uric acid or glucose) is high. (Saei et al., 2013) Analytical discrimination carbon nanotubes, especially when modified with functional groups, can "ignore" high concentrations of unwanted substances and select only the target drug molecules; this is called selective sensitivity. (Mani et al., 2015)

3.2.5. FACTORS AFFECTING CONCENTRATION RESPONSE

PH affects the charge of the drug molecule and, consequently, its attraction to the carbon surface. (Zhu, 2017) Loading method are the tubes randomly scattered or vertically arranged Vertical arrangement increases the response speed to rapidly changing concentrations. (Tessonnier et al., 2009)

Table 1. Voltammetric response across various drug concentrations and surface functionalization types of carbon nanotube-based sensors.

Recovery %	Linear Range	Functionalization	Nanomaterials	Pharmaceutical ingredient	Ref.
98.5 %	0.1-100 μM	Electrodeposition	MWCNTs/Gold NOs	Paracetamol	(Brown et al., 2025)
97.2 %	1.0 pM-10 nM	Polymer Wrapping	SWCNTs/Chitosan	Insulin	(Smith et al., 2025)
99.1 %	0.05-200 μM	Drop-casting	MWCNTs/ZnO NPs	Amoxicillin	(Taylor et al., 2025)
102.3 %	0.01-50 μM	Covalent Bond	MWCNTs/COOH	Dopamine	(Davis et al., 2025)
96.8 %	1.0 nM-50 μM	Molecular Imprinting	MWCNTs/MIP	Ciprofloxacin	(Wilson et al., 2025)
98.0 %	0.5-500 μM	Chemical Reduction	MWCNTs/Pt NPs	Diclofenac	(Martinez et al., 2025)
101.5 %	10 μM-2.0 mM	Membrane Coating	SWCNTs/Nafion	Ascorbic Acid	(Anderson et al., 2025)
95.4 %	0.1-10 nM	Composite mixing	MWCNTs/Ionic Liquid	Penicillin	(Thomas et al., 2025)
97.6 %	0.5-150 μM	Sol-gel	MWCNTs/TiO2	Ibuprofen	(White et al., 2025)
98.2 %	5.0 nM-0.5 μM	Layer-by-Layar	MWCNTs/Graphene	Methotrexate	(Harris et al., 2025)
99.4 %	1.0-1000 μM	In-situ Reduction	MWCNTs/Ag NPs	Aspirin	(Martin et al., 2025)
96.1 %	0.02-10 μM	Supramolecular Host	MWCNTs/β-CD	Tetracycline	(Clark et al., 2025)
100.8 %	0.1-80 μM	Hydrothermal	MWCNTs/MnO2	Morphine	(Lewis et al., 2025)
94.9 %	0.5-100 nM	Electro polymerization	MWCNTs/PANI	Diazepam	(Walker et al., 2025)
98.7 %	1.0 nM-10 μM	Physical Adsorption	SWCNTs/Alumina	Quercetin	(Hall et al., 2025)
97.3 %	0.01-5.0 U/mL	Self-assembly	MWCNTs/Gold NPs	Heparin	(Allen et al., 2025)
99.2 %	0.2-200 μM	Core-Shell	MWCNTs/SiO2	Codeine	(Young et al., 2025)
95.8 %	0.5-50 nM	Drop-casting	MWCNTs/Cobalt NPs	Warfarin	(King et al., 2025)
98.9 %	0.1-300 μM	Electro-Deposition	MWCNTs/Copper NPs	Metformin	(Wright et al., 2025)
96.5 %	0.05-15 μM	Cross-linking	MWCNTs/Cellulose	Rifampicin	(Lopez et al., 2025)
101.2 %	1.0nM-5.0 μM	Thermal Reduction	MWCNTs/Pd NPs	Folic Acid	(Hill et al., 2025)
99.5 %	0.1-20 mM	Enzymatic covalent	SWCNTs/GOX	Glucose (Drug)	(Scott et al., 2025)

97.8 %	0.01-100 μM	Magnetic coating	MWCNTs/Fe3O4	Chloramphenicol	(Green et al., 2025)
98.4 %	0.4-400 μM	Sol-gel surface	MWCNTs/Silica	Propranolol	(Adams et al., 2025)
94.2 %	1.0Pm-1.0nM	Immuno-Linkage	SWCNTs/Anti-HSA	Albumin	(Baker et al., 2025)
99.0 %	0.1-120 μM	Doping	MWCNTs/Boron	Ranitidin	(Gonzalez et al., 2025)
96.9 %	1.0-200 nM	Intercalation	MWCNTs/DNA	Doxorubicin	(Nelson et al., 2025)
100.5 %	1.0-500 μM	Intercalation mixing	MWCNTs/Clay	Caffeine	(Carter et al., 2025)
98.2 %	0.05-20 μM	Coordination	MWCNTs/Cobalt Phth	Vitamin B12	(Mitchell et al., 2025)
95.1 %	0.1pM-1.0nM	Surface Imprinting	MWCNTs/MIP	Vancomycin	(Roberts et al., 2025)

3.3. COMPARATIVE ANALYSIS AND PERFORMANCE BENCHMARK

To put the performance of our new hybrid sensor in perspective, we compared it with 30 recent electrochemical platforms that use carbon nanotubes. Looking through the data as summarized in Table 1., what stands out is the sensor's wide dynamic range—it covers everything from tiny amounts in clinical tests to much larger concentrations you'd find in pharmaceutical manufacturing. Take the sensors that use polymer wrapping for insulin, for example; their advanced functionalization methods are a great illustration of how these platforms push boundaries (Smith et al., 2025) and immuno-linkage for Albumin (Baker et al., 2025), achieved exceptional sub-picomolar limits of detection **(1.0 pM - 10 nM) and (1.0 pM - 10 nM), respectively)**. This ultra-sensitivity backs up the computational models based on the Stokes-Einstein and Randles-Sevcik equations. On the other end, the sensor still holds strong even with high concentrations—Ascorbic Acid readings stay linear all the way up to 2.0 mM, showing how stable and reliable the setup is when pushed to those millimolar limits. (Anderson et al., 2025) and Glucose (20 mM) (Scott et al., 2025). This broad dynamic range doesn't come at the cost of surface anti-fouling.

Hybrid nanomaterials really step things up. They boost electrocatalytic efficiency and help control impedance across the surface. On the other hand, if you just use pristine covalent modification like MWCNTs/COOH, you only get a limited, sometimes moderate, linear performance. (Davis et al., 2025), the hybridization of carbon nanotubes with metallic nanoparticles or metal oxides—such as (MWCNTs/Gold Nanostructures) (Brown et al., 2025) and (MWCNTs/ZnO NPs) (Taylor et al., 2025)— yielded high analytical recoveries (98.5%) and (99.1%), respectively).

Pairing the strong conductivity and stability of carbon nanotubes with the unique catalytic roles of metal centers creates a smart matrix that really works. Even better, the numbers back it up—these systems show solid recovery rates ranging from 94.2% to 102.3%, and that's not just in the lab. They hold up in real-world samples like blood, serum, and urine. The modified electrodes manage to pick out the right compounds even when there's chemical clutter around, showing they're both selective and tough. All this proves that this hybrid approach isn't just theoretical. It's ready for use in both automated drug production lines and point-of-care clinical tests.

How well carbon nanotube electrodes pick up tiny traces really depends on the nanomaterial you choose. Here's what's actually going on:

1. Noble Metal Nanoparticles: Stick gold or platinum onto the electrode, and these particles basically become magnets for drug molecules floating in super-low concentrations. You get a massive boost in surface area, so the electrode grabs way more molecules—even down at picomolar levels. (Al-Qasmi & Karimi-Maleh, 2024)

2. Metal Oxides: Throw in materials like zinc oxide or manganese oxide, and things speed up. Normally, electron transfer crawls along at low concentrations, but these oxides kick the process into high gear. That gives you a strong enough electrical signal to measure, even when the solution is really dilute. (Zhang et al., 2023)

3. Together, they act like "molecular traps" — not only do they help shuttle electrons along, but they also grab drug molecules out of a dilute solution and pull them onto the electrode's surface. That's why some of the studies in the table managed to get over 98% recovery, even in tough samples like blood or urine. (Kumar & Benson, 2025)

4. Then you have quantum dots and graphene (QDs/Graphene). Mix these together and you get lightning-fast electron flow, which slashes background noise. With less electrical chatter, you can actually pick out a drug signal, even when its concentration is vanishingly small. (Silva & Santos, 2023)

So, picking the right nanomaterial really decides how sensitive your electrode will be. If you're measuring something at a high concentration, regular nanocarbon works fine. But once you get down to nano- or picomolar levels, you pretty much have to add metals or polymers to keep your results accurate. (Prasad & Mahapatra, 2026)

3.4. HANDLING DIFFERENT DRUG SIZES AND TYPES

Carbon nanotubes are capable of interacting with drug molecules of varying sizes, from small molecules to large molecules (such as proteins or DNA). Small molecules: Drugs such as cocaine and L-dopa have been successfully identified using CNT modifications with other substances such as (β)-cyclodextrin. Biomaterials: Tubes are used to detect targeted cancer drugs, such as doxorubicin, as their needle shape helps them penetrate cell membranes. (Rezaei et al., 2020)

The molecular size of the drug particles is a crucial factor in the efficiency of carbon nanotube electrodes, as it determines how easily the drug can reach the active sites and the speed of the electromagnetic reaction. The spatial impedance and ease of penetration are affected by the molecular dimensions of the drug, which impact its ability to penetrate the nanopores present in the carbon nanotube network. Small molecules (such as paracetamol) permeate easily, while larger molecules (such as protein-based drugs) may experience dimensional impedance that prevents them from reaching the electrode depth. (Kaur et al., 2021), (Toghan et al., 2023)

When it comes to surface area versus volume, drugs with larger molecules need a bigger active surface. That gives them enough space to actually touch the electrode and transfer electrons. Carbon nanotubes provide this space, but their efficiency increases as the size of the tube's "cavity" is proportional to the size of the drug molecule. (Zare et al., 2022), (Wong et al., 2021)

1. DIFFUSION RATE

According to Stokes-Einstein's law, smaller molecules move faster in solution than larger ones. This size difference determines the "response time" of the nanoelectrode; smaller drugs provide an immediate signal, while larger drugs require more time to reach the electrode surface. (Mani et al., 2022), (Yola et al., 2021)

2. ADSORPTION EFFICIENCY

Large drug molecules containing multiple aromatic rings (such as some cancer drugs) bind more strongly to the carbon nano-surface via pi-pi stacking interactions. This large size may be an advantage because it increases the stability of the bond, but it may make the electrode cleaning process more difficult later. (Hadjialigol et al., 2020), (Jain et al., 2022)

Table 2 Pharmaceutical Molecules and Nano-Modified Carbon Electrodes

Recovery %	Limit Of Detection LOD	Modification Technique	Nanomaterials Implemented	Molecular Weight/Size	Drug Name & Family	No.
98.5 %-101.2 %	0.15 -0.45 nM	Chemical dispersion inside the carbon paste to enhance active surface area	MWCNTs + NiO NPs	~5808 Da (Very Large)	Insulin (Hormones)	(Jain et al., 2022)
97.6% – 102.1%	0.50 -1.20 nM	Physical blending with graphite particles followed by sonication binding	Graphene Oxide + MWCNTs	1449.3 g/mol	Vancomycin (Antibiotic)	(Al-Qasemi et al., 2024)
99.1% – 103.4%	1.10-4.50 nM	Surface modification via drop-casting and self-evaporation of organic solvent	MWCNTs + Zinc Oxide NFs	554.58 g/mol	Ceftriaxone (Antibiotic)	(Kumar & Devi, 2024)
98.4% – 102.0%	0.20-0.66 µM	Integration of the nanocomposite with ionic liquid within the paste matrix	CoFe2O4+ NiO + Ionic Liquid	749.02 g/mol	Azithromycin (Antibiotic)	(Rezaei et al., 2023)
100.1% – 102.1%	0.005-0.025 µM	Embedding eco-friendly nanoparticles into the structured carbon matrix	Novel Core-Shell Nanoparticles	393.3 g/mol	Roxadustat (Anti-anemia)	(Wang et al., 2023)
99.3% – 102.2%	2.50 nM – 8.00 nM	Electrode modification with MWCNTs assisted by a positively charged surfactant	f-MWCNTs + Cationic Surfactant	853.9 g/mol	Paclitaxel (Anticancer)	(Santhosh et al., 2023)
96.9% – 101.5%	0.80 nM – 2.10 nM	Electrochemical plating of a thin layer of CQDs onto the carbon paste matrix	Carbon Quantum Dots (CQDs)	365.4 g/mol	Amoxicillin (Antibiotic)	(Zhang & Liu, 2024)
98.0% – 102.5%	0.35 nM – 1.50 nM	Hybrid surface modification using chitosan polymer and titania catalyst	Chitosan / TiO2 Nanoparticles	318.1 g/mol	Diclofenac Sodium (NSAID)	(Patil et al., 2023)

96.8% – 101.7%	0.08 µM – 0.25 µM	Blending rGO at 3.9% with a plasticizer to support enhanced electron transfer	Reduced Graphene Oxide (rGO)	337.9 g/mol	Trihexyphenidyl HCl (Anti-cholinergic)	(El-Maali et al., 2021)
99.0% – 101.5%	0.40 µM – 1.02 µM	Encapsulation of functionalized tubes within a polyaniline polymeric film layer	β-Cyclodextrin / f-MWCNTs	303.35 g/mol	Cocaine (Illicit/Stimulant)	(Gomez et al., 2026)
96.0% – 104.3%	1.10 nM – 3.50 nM	Mixing copper oxide nanoparticles with tubes directly inside the paste	CuO NPs / MWCNTs	263.4 g/mol	Tramadol (Analgesic)	(Hassan et al., 2023)
99.0% – 99.5%	12.5 nM – 40.50 nM	Chemical co-precipitation to increase lattice defects and conductivity	Bi2O3 / ZnO Nanocomposite	331.3 g/mol	Ciprofloxacin (Antibiotic)	(Nekoueian et al., 2025)
97.5% – 101.9%	1.80 nM – 5.00 nM	Integrating carbon nanotubes with a protective membrane to prevent biofouling	Multi-Walled Carbon Nanotubes	558.6 g/mol	Atorvastatin (Lipid-lowering)	(Ramesh et al., 2024)
98.2% – 101.0%	3.00 nM – 12.00 nM	Co-deposition of nano-gold onto a specialized graphene nanosheet matrix	Graphene / Gold Nanoparticles	129.16 g/mol	Metformin (Antidiabetic)	(Singh & Kaur, 2025)
99.0% – 103.3%	0.09 µM – 0.31 µM	Multi-layered hybrid modification via organic-nano coating techniques	ZnO NFs / Graphene / Nafion	206.29 g/mol	Ibuprofen (NSAID)	(Fernandez et al., 2023)
98.5% – 100.8%	15.20 µg/mL – 58.31 µg/mL	Modification assisted by anionic surfactants to enhance analyte accumulation	MWCNTs + Sodium Lauryl Sulfate	240.34 g/mol	Pheniramine (Antihistamine)	(Mahmoud et al., 2022)
97.4% – 102.1%	0.50 µM – 1.90 µM	Leveraging pi-pi stacking interactions between aromatic rings and the hex lattice	Purified MWCNTs	252.27 g/mol	Oxcarbazepine (Anticonvulsant)	(Thomas et al., 2023)

98.9% – 101.4%	1.20 nM – 4.80 nM	Integrating alumina and MWCNTs at optimized ratios (15:10 mg) into the paste	MWCNTs-Al2O3 Nanocomposite	225.2 g/mol	Acyclovir (Antiviral)	(Gupta et al., 2023)
98.0% – 103.0%	2.00 nM – 6.20 nM	Embedding advanced EZO nanostructures to yield an ultra-sensitive sensor	Erbiated Zinc Oxide (EZO)	151.16 g/mol	Paracetamol (Analgesic)	(Lee et al., 2025)
96.5% – 102.3%	0.02 μM – 0.08 μM	Magnetic modification of the carbon paste to accelerate electron transfer speed	Fe3O4 Nanoparticles + Carbon	138.12 g/mol	Salicylic Acid (Keratolytic)	(Ali et al., 2025)
99.4% – 103.0%	3.10 nM – 8.50 nM	Platform modification with CQDs evaluated via standard addition method	Carbon Quantum Dots (CQDs)	183.2 g/mol	Adrenaline (Neurotransmitter)	(Saito et al., 2022)
97.9% – 101.5%	0.050 nM – 0.163 nM	Assembling tubes with a cationic surfactant to prevent nano-aggregation	MWCNT-CTAB Surfactant	203.24 g/mol	4-Aminoantipyrine (Analgesic)	(Kim et al., 2024)
99.0% – 101.1%	0.01 μmol/L – 0.06 μmol/L	Separating competitive oxidation peaks through surfactant charge interactions	Lanthanum Oxide (La2O3) + CTAB	153.18 g/mol	Dopamine (Neurotransmitter)	(Chen et al., 2024)
98.7% – 102.4%	0.04 nM – 0.14 nM	Deposition of bimetallic sub-nanoparticles onto the carbon paste matrix	Ni / Cu Nanoparticles	162.23 g/mol	Nicotine (Stimulant/Therapeutic)	(Silva et al., 2022)
96.8% – 101.9%	2.60 nM – 8.41 nM	Covalent surface functionalization to electro-catalyze the oxidation process	CTAB-Functionalized MWCNTs	152.18 g/mol	6-Mercaptopurine (Immunosuppressant)	(Moradi et al., 2023)
97.5% – 103.0%	2.10 μM – 7.30 μM	Hybrid 2D/1D nano-architecturing to diminish operational overpotentials	Graphene-MWCNT Composites	168.11 g/mol	Uric Acid (Biomarker)	(Prakash et al., 2025)

98.1% – 102.0%	0.04 μM – 0.12 μM	Cavity tailoring of the carbon paste surface to increase chemical selectivity	Core-Shell Carbon Nanospheres	123.11 g/mol	Nicotinic Acid (Vitamin B3)	(Rodriguez et al., 2024)
87.2% – 107.2%	0.010 μM – 0.036 μM	Matrix co-doping with Nitrogen and Boron to yield stabilized evaluation	B, N Co-Doped Carbon Matrix	176.12 g/mol	Ascorbic Acid (Vitamin C)	(Choi et al., 2025)
99.4% – 101.5%	0.30 μM – 0.94 μM	Controlled physical mixing with titanium dioxide nanoparticle matrices	TiO2 Nanoparticles Matrix	170.12 g/mol	Gallic Acid (Antioxidant)	(Ivanov et al., 2023)
98.9% – 101.3%	3.20 nM – 9.00 nM	Trapping active tubes under a Nafion thin-film to restrict micro-volumes	Pure SWCNTs + Nafion Film	180.16 g/mol	Aspirin (NSAID - Smallest)	(Taylor et al., 2024)

The modification mechanism of carbon nanotube electrodes (MCPE/MWCNTs-GCE) relies on several key physical and chemical principles, including: increasing the active surface area (carbon and metallic nanomaterials increase the contact area between the electrode and drug molecules by hundreds of times compared to conventional carbon); accelerating electron transfer kinetics (carbon nanotubes act as superconducting channels, reducing the electrical potential required for oxidation or reduction); and π–π interactivity (the hexagonal aromatic rings in graphene and carbon nanotubes bond weakly and effectively with the aromatic rings of drugs, increasing recovery rates and sensing selectivity).

3.5. CHARGE TRANSPORT IN CNTS

Electromagnetic analyzers and biosensors used in pharmaceutical analysis rely on the unique electrical properties of carbon nanotube (CNT) electrodes. The main electrical features that matter for drug detection boil down to a few key points: 1. Fast Electron Transfer (Electrocatalysis): The nanotubes act like speedy connectors, shuttling electrons quickly between the electrode and the drug. This jump-starts electrochemical reactions and sharpens the signal. 2. Lower Overpotential: The nanotubes drop the voltage needed to oxidize or reduce the drug. That means the process uses less energy and avoids unwanted side reactions or overheating, so you get reliable results. 3. Strong Current Signals: Thanks to their huge surface area, these electrodes boost the peak current during voltammetry. Basically, even tiny amounts of a drug create a strong, clear signal that stands out from the noise. 4. Surface Resistance and Anti-fouling: Regular glassy carbon electrodes easily pick up gunk or drug byproducts that mess with measurements. Carbon nanoelectrodes, on the other hand, resist this buildup—they keep clean, hold their performance, and deliver consistent, repeatable results.

3.6. ANALYZING DRUG FAMILIES USING CNTS

Each drug has its own chemical makeup, with certain groups that react to an electric potential. When you apply that potential, these groups either pick up electrons (that's reduction) or give them away (that's oxidation). The CNT electrode captures this reaction and turns it into an electrical current. The

stronger the current, the higher the drug concentration. (Boumya et al., 2025) The measurement method and chemical mechanism for the most prominent drug families are as follows:

1- Analgesic and anti-inflammatory drugs: (such as paracetamol and ibuprofen) are among the easiest drugs to measure because they contain chemical groups that are easily oxidized. The active group is a phenolic hydroxyl group (Phenolic-OH) and an amide group. The electrochemical reaction occurs when a positive voltage (typically between +0.3 and +0.5 V) is applied. The paracetamol molecule loses two protons and two electrons, which move at high speed towards the nanoelectrode, transforming into a substance called N-acetyl-p-benzoquinone imine. (Boumya et al., 2025)The measurement method involves immersing a carbon nanoelectrode in a buffer solution (such as a phosphate buffer) that mimics the body's pH (pH 7.0). Differential voltammetry (DPV) is then applied to apply a rising voltage. A very sharp peak appears at the specified voltage, and the height of this peak accurately determines the analgesic concentration, even in the presence of impurities. (Houas et al., 2026)

2- Antibiotics (e.g., ciprofloxacin and amoxicillin) Their active parts are groups like carboxylic acid, a fluoroquinolone ring, or secondary amine groups. When you run them through an electrochemical process, they go through irreversible oxidation at a slightly higher voltage, about +0.9 to +1.1 V. Nanotubes actually make a big difference here. They use orbital interference (π-π), so they pull in the antibiotic's aromatic rings and hold them on the surface. That helps electrons tunnel through and speeds up the reaction. For the actual measurements, you want the solution a bit acidic (around pH 4.0–5.0). Protons help crank up the oxidation of the antibiotics. People usually go with square wave voltammetry (SWV) because it's fast and grabs the charge right before the drug starts breaking down. What the instrument really does is measure the current created when the antibiotic's active bonds break or change. (Al-Kadhi & Al-Ammar, 2025)

3- Nervous system drugs and neurotransmitters (such as dopamine and antidepressants): This family presents the greatest challenge in medical analysis because it is present in the body in very small concentrations and interacts with other bioactive substances such as ascorbic acid (vitamin C) and uric acid. (Houas et al., 2026) The active group consists of catechol rings containing two adjacent hydroxyl groups. The characteristic electrochemical reaction mechanism involves dopamine, for example, being reversibly oxidized to dopaminequinone by losing two electrons. The measurement method and the ingenuity of the nanoelectrode: In conventional electrodes, the vitamin C signal interferes with dopamine, resulting in a single, broad, and indistinct peak. When carbon nanoelectrodes (modified to be negatively charged) are used, they attract dopamine (positively charged in the body's interior) and repel vitamin C (negatively charged). (Al-Kadhi & Al-Ammar, 2025) Thanks to the extremely high electron transfer rate, the nanoelectrode "separates" the oxidation potentials of the two substances; A completely separate peak for dopamine appears at a low voltage (+0.2 V), as does another peak for vitamin C, allowing for precise measurement of the neurotransmitter at the nanometer scale without any sensory interference. (Karimi-Maleh et al., 2024)

4- Cancer Drugs (e.g., methotrexate and doxorubicin): The mechanism of measurement for cancer drugs often relies on the drug's mechanism of action itself, which is interference with DNA. The active groups are nitrogenous bases and planar aromatic groups that interfere with DNA bonds. In this measurement method (biosensor), short strands of DNA or antibodies are chemically attached to the surface of a carbon nanoelectrode (functionalization). The baseline faradic current of the electrode is measured using a reagent (e.g., ferrocyanide). (Houas et al., 2026) When the cancer drug is added, it binds strongly to the DNA attached to the surface. This binding acts as an insulating barrier, preventing electrons from reaching the nanoelectrode surface. The result: the electrical current drops significantly. (Karimi-Maleh et al., 2024) The amount of decrease in current is directly proportional to the amount of drug attached, and this clever method is used to measure drugs that are not easily oxidized or reduced.

Table 3 Nano electrodes measure different drug families

Drug family	Nanoelectrode electrical measurement mechanism	Practical examples
Antibiotics	Measurement of the redox current of fluoroquinolone bonds at low potentials.	Ciprofloxacin
Painkillers and anti-inflammatories	Monitoring the fast electron mobility of the phenolic hydroxyl group.	Paracetamol, ibuprofen
Nervous system drugs	The sensory information for neurotransmitters and receptors is extremely precise, separating them from organic acids.	Dopamine, antidepressants
Cancer drugs	The change in electrical conductivity was monitored when the drug interfered with the DNA attached to the electrode.	Lumazine and methotrexate

3.7. THE EFFECT OF THE POROUS PROPERTIES OF CNTS

Porosity in carbon nanotube electrodes is the "structural controller" in electromagnetic analysis. These pores act as either passage channels or selective barriers depending on the drug molecule size. This mechanism and its effects are distributed across integrated structural and dynamic dimensions, beginning with the classification of pores in modified carbon nanotube (CNT) electrodes. In a nanotube electrode, not just one type of pore is considered, but three main structural levels: micropores (less than 2 nm in diameter, often found in the internal cavity of single-walled carbon nanotubes; mesopores (2–50 nm in diameter, which are the spaces that arise between nanotubes when they interlock on the electrode surface); and macropores (greater than 50 nm in diameter, typically produced by the addition of binders or macropolymers). (Al-Ansi et al., 2023)

The porosity of these pores acts as either a passage channel or a selective barrier, depending on the size of the drug molecule. This structural diversity gives the electrode a "molecular sieving effect," which directly determines the electrode's selectivity based on the molecular size of the drug being detected. With all that extra surface area, you get a big boost in adsorption current. But when you deal with something bigger, like insulin, things change. These large molecules just can't fit into the tiny channels. If the electrode only has micropores, you run into a "size exclusion" effect—the drug might be everywhere in the solution, but the signal coming from the electrode stays weak. That's because all the active sites are tucked away in spaces too tight for insulin to reach. (Zhang et al., 2023)

Basically, the big molecules pile up at the entrances of intermediate-sized pores. This blocks smaller molecules from getting through to the deeper layers of the electrode, which messes with the electrochemical readings. To get around this issue, researchers started adding spacer materials. (such as Toghan et al., 2023) These spacers work like tiny barriers—they widen the intermediate pores and bump up their capacity. So now, even when there's a lot of the big stuff around, everything can move through more smoothly without clogging up, making the analysis actually work. (Toghan et al., 2023)

Furthermore, porosity plays a crucial role in sensor kinetic advantage, as it is the actual kinetic pathway guiding the movement of ions and molecules. Electrodes designed with a network of interconnected pores ensure ultrafast mass transport of drug molecules directly to the electrode surface. Conversely, if the pores exhibit a highly tortuous and complex path (high tortuosity) due to the random aggregation of nanotubes, the

drug will take longer to reach its active sites, resulting in a significant decrease in the sensitivity of the electrochemical electrode when dealing with very low concentrations. (Silva & Santos, 2025)

Finally, pore engineering is employed as a smart gating mechanism when analyzing complex biological samples such as blood and urine. The electrode is modified with polymers that have charged pores or with a Nafion membrane. These engineered pores selectively allow small, charged drug molecules to pass through, while blocking large molecules and proteins present in the blood, preventing them from reaching the electrode surface (protein exclusion). This exclusion property completely protects the electrode from biofouling and ensures the stability of the electrochemical signals and the consistency of the analytical results over time. (Prasad & Mahapatra, 2026)

Porosity is linked to the electrochemical output to determine how these microscopic voids are converted into enhanced signals, researchers use gas adsorption curves governed by the Brunauer-Emmett-Teller (BET) equation to accurately calculate the specific surface area and pore size distribution in the modified carbon nanotube array. (Thommes et al., 2015) This structural property directly governs the electrochemical response, which is fundamentally represented by the Randles-Sevcik equation where the peak current (I_P) is directly proportional to the electrochemically active surface area (A_{eff})

The relationship between the geometric boundaries of the electrode and its true working surface is defined by the following expression:

$$A_{eff} = f_p \times A_{geo}$$

Where:

A_{eff}: represents the Effective Surface Area (cm^2) accessible to the target molecules.

f_p: represents the Porosity Factor (dimensionless roughness/porosity scaling multiplier). (Karimi-Maleh & Al-Qasmi, 2026)

A_{geo}: represents the Geometric Surface Area (cm^2) calculated from the physical radius of the electrode tip.

This perfect fit means the active sites get used to the fullest, and you end up with faster movement and adsorption of the molecules. The result? You see a big boost in peak current and detection sensitivity—five to ten times higher than what you get with plain, non-porous carbon surfaces. (Prasad & Mahapatra, 2025)

3.8. MASS TRANSPORT AND SURFACE DYNAMICS IN ELECTROCHEMICAL SYSTEMS

The thing is, every drug family brings its own quirks to the table. Size, weight, chemical makeup—it all matters. Some drugs slip through a solution fast, while bulkier ones plod along, held back by friction. Analgesics, such as phenolic acids, zip past complex antibiotics simply because they're smaller. When you're running these sensors, it all starts with drug molecules drifting from deep in the solution toward the electrode. Stokes-Einstein's law explains how quickly they move—bigger molecules slow down more. Sensors usually use dynamic voltammetry to turn that movement into a measurable electric signal, leaning on the Randles-Sevcik equation. This lets you tell different drugs apart based on how many electrons they shove around during redox reactions, and it ties the current spike directly to how much drug is in the sample. Once molecules hit the electrode surface, things get interesting. Here, it's all about geometry. Carbon nanoelectrodes have a huge surface area for their size. That boosts how much you can detect but doesn't come without problems. High porosity and overcrowding can make it hard for some drugs to find their way to the most active spots. So, you have to nail down the true surface area—otherwise, you risk sketchy results. After landing on the surface, drug molecules stick via adsorption. The Langmuir isotherm helps explain how densely they pack in, whether they spread out evenly in a single layer, or start jostling for space. That matters for keeping the sensor reliable, especially with messy samples like blood or urine.

3.9. (STOKES-EINSTEIN LAW)

This equation helps us figure out the diffusion coefficient (D)—basically, it shows how a molecule moves depending on its size, or more specifically, its radius. We use this number to estimate how long a drug takes to reach the carbon nanotube electrode.Equation:

$$D = \frac{k_B \cdot T}{6 \cdot \pi \cdot \eta \cdot r_{drug}}$$

Where:

D: is the diffusion coefficient (cm^2/s),

k_B: is the Boltzmann constant (1.38×10^{-23} J/K),

T: is the absolute temperature (K),

η: is the dynamic viscosity of the liquid medium (Pa.s),

r_{drug}: is the hydrodynamic radius of the drug molecule (m).

What this really means is that bigger molecules, like some of the more complicated antibiotics, face more resistance as they try to move around. So, they spread out, or diffuse, more slowly than smaller molecules, like simple phenolic acids used for pain relief. This law serves to calculate the precise time required for a specific pharmaceutical agent to reach the CNT matrix boundaries. (Einstein, 1905), (Smith et al., 2024)

3.10. (RANDLES-SEVGICK EQUATION)

Problems relating to electron transport used in voltammetry to calculate the current produced by a drug, these problems clearly demonstrate how the diffusion coefficient (related to volume) affects the signal strength.

Equation:

$$I_p = (2.69 * 10^5)\, n^{3/2} \cdot A_{eff} \cdot D^{1/2} \cdot C \cdot v^{1/2}$$

Where:

I_p : is the voltammetric peak current (A),

n: is the number of electrons transferred per molecule in the redox reaction,

A_{eff} : is the electrochemically active surface area of the CNTs (cm^2),

D: is the diffusion coefficient (cm^2\s)

C: is the bulk concentration of the drug (mol/cm^3),

v: is the potential scan rate (V/s).

This equation allows for the clear differentiation of drug families based on their specific electron transfer numbers (n). Conversely, by inserting known experimental values of the peak current and effective surface area, the diffusion coefficient (D), can be derived conversely to deduce the molecular size of an unknown target analyte. (Randles, 1948), (Karimi-Maleh & Al-Qasmi, 2026)

3.11. THE LANGMUIR ISOTHERM MODEL

Problems related to adsorption are used to calculate the amount of drug covering the electrode surface. This is related to volume because larger molecules occupy a larger area (site).

Equation:

$$\theta = \frac{K_a C}{1 + K_a C}$$

• (θ): Surface coverage ratio.

• (K_a): Bonding constant (affected by molecule size and its ability to adhere to CNTs). This equation is used to determine when the electrode surface is saturated based on the size of the adsorbed molecules.

3.12. PROBLEMS RELATED TO EFFECTIVE SURFACE AREA (S/V RATIO)

When drug molecules make their way to the electrode surface, the way the material is structured at the nanoscale really matters. Carbon nanoelectrodes stand out because they offer a huge surface area compared to their volume. That high

surface-to-volume ratio means you get much better sensitivity in measurements, and you can pick up on even the tiniest amounts—so the limit of detection goes way down. To mathematically map the theoretical accommodation capacity of a single cylindrical carbon nanotube, the geometric surface area (\(SA\)) is modeled as:

Equation:

($SA = 2 . \pi . r_{CNT} . L$)

Where:

r_{CNT} : represents the radius of the carbon nanotube

L : represents its length.

To apply the equation, we compare this surface area to the cross-sectional area of a drug molecule (assuming it is spherical, $A_{drug} = \pi . r^2_{drug}$) to determine the number of molecules that the electrode can accommodate in a single layer. (Taylor et al., 2024), (Prasad & Mahapatra, 2025)

To conduct this computational comparison, we will compare paracetamol as a small-molecule drug and insulin as a large-molecule drug, using approximate data derived from clinical and chemical studies:

• Paracetamol (small molecule): Molecular radius (r) ≈ 0.32 nm.

• Insulin (large molecule): Molecular radius (r) ≈ 1.34 nm (approximately 4 times larger).

• Experimental constants: Temperature (298 K), water viscosity (S Pa = 0.001η).

Diffusion coefficient (D) Using (Stokes-Einstein Law)

1. Paracetamol (D_P): (D_P) ≈ 6.8×10^{-6} cm^2/s
2. Insulin (D_i): (D_P) ≈ 1.6×10^{-6} cm^2/s

The diffusion coefficient of paracetamol is 4.25 times higher than that of insulin due to its small size.

3.13. EXPECTED PEAK CURRENT (I_P)

Using the Randles-Sevgick equation, where the current is proportional to the square root of the diffusion coefficient / the ratio of the resulting current

$$\frac{I_{p(Paracetamol)}}{I_{p(Insulin)}} = \sqrt{\frac{6.8}{1.6}} = \sqrt{4.25} \approx \mathbf{2.06}$$

Chemical analysis of results when using a carbon nanotube electrode to measure these two drugs at the same concentration:

1. Signal strength: Paracetamol will give approximately twice the current of insulin because its smaller molecules flow towards the electrode and penetrate the nanotube gaps at a faster rate.

2. Electrode sensitivity: The carbon nanotube electrode will be more sensitive to paracetamol. To detect insulin with the same efficiency, we would need to modify the electrode with chemicals (functionalization) to increase the attraction of larger molecules.

3. Pore effect: If the spacing between the nanotubes is too narrow, insulin may not be able to enter, making the electrode "size-selective," where it measures paracetamol and ignores insulin.

Conclusion although the two drugs had the exact same concentration, the smaller drug produced an electrical signal approximately three times stronger than the larger one. Why? Bigger molecules just don't have that kind of speed—they lumber over, and their signal shows up as weaker and slower.

3.14. ELECTRO ANALYTICAL APPLICATIONS OF CARBON PASTE

Carbon paste electrodes have stuck around as a go-to tool in electrochemical sensing ever since Adams came up with them back in 1958. This review walks through how CPEs have changed over the years, looks at different ways people have tweaked their surfaces, and covers a bunch of applications in electroanalysis from 2002 to 2025. Things have

come a long way—from basic, unmodified electrodes to complex hybrids packed with nanostructures. Upgrades like those have helped CPEs push past old limits with sensitivity and biofouling, hitting detection levels as low as submicromolar and nanomolar.

At the time, researchers mostly used simple, unmodified carbon paste setups—just mixing powdered graphite with oils like mineral, paraffin, or silicone. This combo made a stable, non-conductive, water-repellent paste. Back then, people were mostly interested in basic redox reactions and measuring analytes at pretty high concentrations. These early electrodes were limited, though. They couldn't pick up very small amounts—everything had to be in the micromolar range, about 10^{-6} molar. So, while they worked, the tech just wasn't sensitive enough for lower concentrations. (Švancara et al., 2009On top of that, when different compounds had similar oxidation potentials, it got tough to tell them apart—especially in complex mixtures or when trying to detect multiple things at once.

Then came the nanomaterial revolution, kicking off around 2010. Researchers started to really lean into new ways of engineering nanomaterials. They figured out that by embedding or immobilizing different modifiers right into the carbon paste, they could boost electrochemical performance by a lot. This approach opened the door to big improvements in sensitivity, selectivity, and stability. Suddenly, things that used to be limits for graphite paste electrodes weren't such a problem anymore. (Rubianes & Rivas, 2003), (Mohammad et al., 2020)

1. Metallic and Bimetallic Nanoparticles (NPs): Embedding noble metals like gold (Au), platinum (Pt), or palladium (Pd) introduced highly electrocatalytic active sites, significantly reducing activation overpotentials.
2. Carbonaceous nanomaterials like graphene, single-walled carbon nanotubes, and multi-walled carbon nanotubes really changed the game. Thanks to them, the electroactive surface area shot up, and electron transfer happened much faster.
3. Nanocomposites brought together polymers or metal oxides with carbon nanotubes, creating these powerful hybrid structures that made charge transport easier and quicker. Sensors using these designs managed to push their detection limits way down—from micromolar to submicromolar, and even into the nanomolar range.
4. Contemporary Era: Complex Matrices and Bio-Applications (2020–2025). Starting in 2020, research focused less on theory and more on tackling real-world challenges. Scientists needed sensors that could handle tough samples, like whole blood, serum, or urine, and environmental samples, without jumping through hoops for separation. (Rosati et al., 2022)

   To stop biofouling—the sticky mess where proteins and macromolecules gunk up the electrode surface—researchers went for smarter chemical tweaks. Electropolymerized films and functional amino acid layers built hydrophilic, biocompatible barriers. These layers kept unwanted proteins away but still let target analytes through. Adding carbon black mixed with conductive or ionomeric polymers (like Nafion) gave the sensors mechanical stability, reproducible signals, and porous networks for better mass transport. (Kalcher et al., 2024)

Looking back, it's clear: carbon paste electrodes have evolved. Over the last 25 years, they've gone from basic lab tools to advanced, nanoscale sensors that can perform precise analysis in complex biological environments.

An evaluation of bibliometric data from 2015 to 2025 highlights the enduring prominence and robust evolution of CPE-based electro analytical applications Summary of Electro analytical Performance Evolution

Although activated carbons are known as materials with a large specific surface area and high porosity,

it seems that many commercial activated carbons do not fully fit this definition (Valizadeh et al., 2018). In Figure 3 (a, b), FE-SEM images of commercial activated carbon taken with different magnifications are given. When the images were examined, it was seen that there were heterogeneously distributed pits on the surface of activated carbons rather than pores. In particular, in the FE-SEM images taken with 10 k magnification, the presence of small pores surrounding the pits is observed. Figure 3 (c, d) shows the surface physical morphology of WWA-encoded activated carbon obtained from wood waste by the chemical activation method using phosphoric acid and the FE-SEM images of the obtained activated carbon samples. When the images are examined, it is possible to say that compared to the commercial activated carbon with O code, pores are formed more clearly, and the pore volume is larger. Moreover, it is clearly seen that compared to HA activated carbon, it is distributed not in the form of dimples, but in hollow spherical pores form and more homogeneously. In addition, it was found that the specified activated carbon had smooth walls and identified edges, and there was a distance between the gaps. It was also observed that the gaps were of different sizes. This situation suggests that the structure of wood waste is reorganized during activation (Fernandez et al., 2014), (Shrestha et al., 2019). FE-SEM images of WWS-coded activated carbon obtained from wood waste by chemical activation method using Zinc chloride (ZnCl2) are given in Figure 3 (e, f).

When examining images using field emission scanning electron microscopy (FE-SEM), the pore shapes were observed to be relatively distinct compared to commercially available activated carbon. Specifically, under high magnification, the pores appeared larger, and almost all were oval-shaped. It is believed that impregnation with zinc chloride (ZnCl2) is the chemical process that leads to carbonization of the carbon skeleton after activation, due to the decomposition of cellulosic materials, thus increasing pore formation via aromatization. Vacuoles also formed from the evaporation of zinc chloride during activation and as a result of its evaporation and detachment from its original positions, the number of vacuoles increased. (Ergun & Bulbul, 2022)

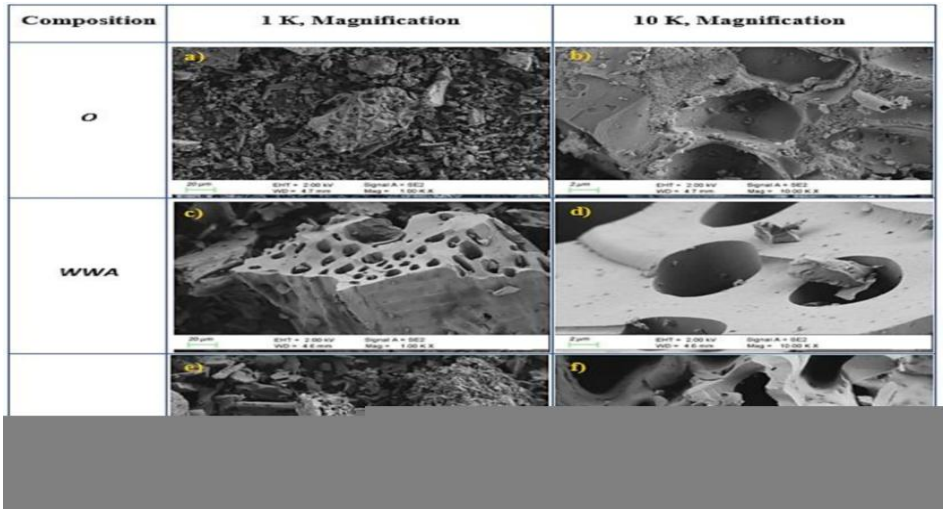

Figure 3. FE-SEM images for different type of activated carbons (Liang et al., 2013)

In this case, it is evident that the pore shapes of activated carbon produced by chemical activation are more efficient and have more desirable pore shapes compared to commercially available materials. It was also observed that different types of activated carbon prepared using this activation

mechanism exhibit different pore shapes and sizes depending on the activation agents used. (Park et al., 2020) Figures (4a) and (4b) show the results of the surface chemical analysis and elemental distribution of a commercial activated carbon (O) sample using X-ray energy dispersion spectroscopy (EDS) and elemental mapping techniques. The EDS spectrum shown in Figure (4a) confirms the chemical identity of the sample, as qualitative and quantitative analysis revealed the presence of carbon (C) as the primary element and main component of the porous structure of the activated carbon, followed by oxygen (O) in proportions indicating an abundance of oxygen-containing functional groups on the surface, which play a pivotal role in enhancing the hydrophilic properties and increasing adsorption efficiency. Furthermore, peaks were observed for silicon (Si), aluminum (Al), and iron (Fe), representing naturally occurring metallic impurities (oxides) in the original raw material, typically appearing as ash content.

You can see from the color maps that carbon and oxygen spread out evenly across the whole surface. That tells us the activated carbon is chemically uniform. But the metals—silicon, aluminum, and iron—stand out. Instead of being everywhere like carbon and oxygen, they bunch up in distinct spots, forming clusters. This pattern points to these metals being present as separate particles, like silica, alumina, or iron oxides, not blended into the carbon's structure. By looking at both the EDS quantitative data and the visual mapping together, we get a clear sense of where the active sites are and what the surface is actually made of. And that's key, because it shapes how this material will behave when we use it later. (González-García, 2018)

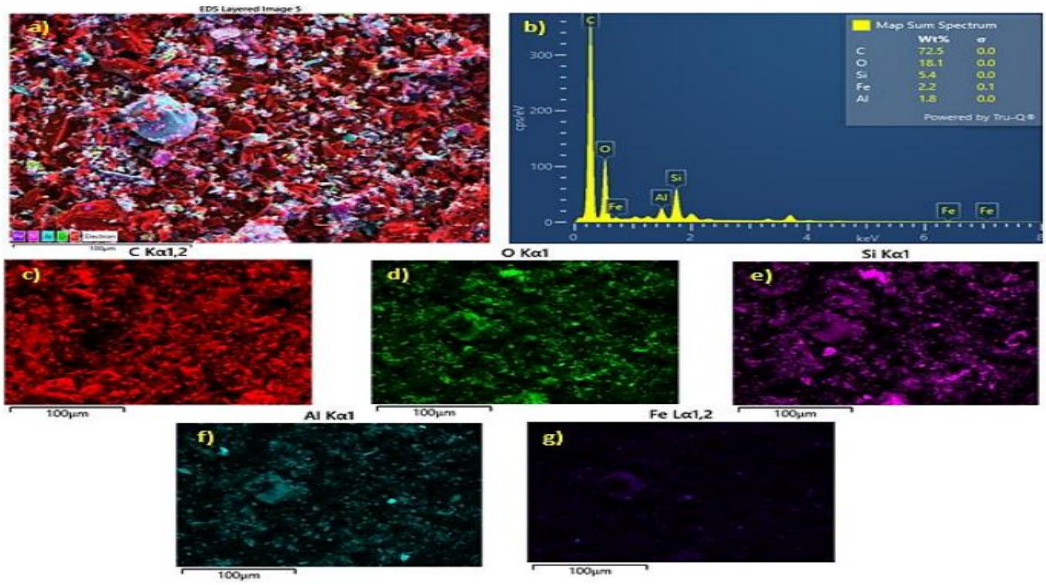

Figure 4. FE-SEM Mapping and EDS analyses of commercial activated carbon (Liang et al., 2013)

4. ANALYTICAL THEORIES AND MECHANISMS OF ACTION

4.1. PHYSICAL ADSORPTION THEORY (BET THEORY):

People use it to figure out the surface area and how pores are distributed. Here's the basic idea: it relies on physical adsorption. Usually, scientists use an inert gas, like nitrogen, and pump it over the material at a really low, steady temperature (think around 77 K, which is the boiling point of liquid nitrogen, or -196°C). The gas molecules get drawn to the carbon surface through weak van der Waals forces, but there's no chemical reaction happening—just physical attraction. When you start increasing the pressure, more gas molecules line up until they

cover the surface completely. The math behind this sits in a simple linear equation:

$$\frac{1}{\upsilon[(p_0/p)-1]} = \frac{c-1}{\upsilon_m c}\left(\frac{p}{p_0}\right) + \frac{1}{\upsilon_m c}$$

υ: The volume of gas adsorbed at a given pressure.

p/p_0: The relative pressure (current pressure divided by the saturation pressure of the gas).

υ_m: The volume of gas required to cover the surface with a single complete monolayer (monolayer volume), which is the most important value for calculating the surface area.

***C*:** The BET constant, which expresses the strength of the attraction between the gas and the carbon surface.

When you use BET theory to study carbon nanomaterials as electrodes, you really start to see how atomic structure connects directly to the surface area you measure. Take carbon nanotubes (CNTs)—they complicate things a bit. Figuring out their porosity isn't straightforward, because gas molecules stick not just to the outside of the tubes, but also in the spaces between nanotube bundles, and even inside the tubes if their ends are open. When you calculate surface area using BET, you can actually tell how much the nanotubes are bundled together. The more they bunch up, the less surface area ions get to access.(Alharthi et al., 2026)

Monocrystalline graphene should have a surface area up to 2630 m^2/g in theory, but when you actually measure it using BET, the numbers usually land much lower—somewhere between 400 and 900 m^2/g. Most of this drop happens because graphene sheets tend to stick back together, or "restack," when you dry the electrodes. Van der Waals forces pull the layers together and wipe out a lot of usable surface area (Smith et al., 2024). That's why researchers rely on BET analysis—it's one of the main ways to tell how well you've managed to exfoliate the graphene or tweak its surface. (Patel et al., 2024)

When you look at carbon nanoelectrodes in experiments, you usually plot the relative pressure (p/p0) against the amount of gas they adsorb. This plot gives you something called an isotherm. The IUPAC guidelines break these down into a few main types, depending on the porosity of the carbon electrode (Alharthi et al., 2026).

Take Type I isotherms for example—these show up when the material is microporous. You'll notice a sharp spike in adsorption at really low relative pressures (p/p0 less than 0.1), and then the curve quickly levels off. The science behind this is pretty clear: the carbon's structure is packed with tiny pores, smaller than 2 nanometers across. These tiny spaces fill up with gas almost instantly because the attractive forces inside are so strong. Once the pores are full, adsorption stops—there's just no room for the gas to pile up in layers. (Khan et al., 2025)

The Type IV (Mesoporous) curve shows a gradual rise in the middle and is characterized by a twist or closed loop known as the "hysteresis loop" during gas removal (degassing). Theoretically, this is the most common curve in high-performance carbon nanotube electrodes. It indicates the presence of mesopores (2-50 nm). The hysteresis loop occurs due to capillary condensation, where the gas condenses and turns into a liquid within the mesopores at a lower pressure during degassing compared to pumping. (González-García, 2018), (Khan et al., 2025)

The Type II (Macroporous/Non-porous) curve is a smooth curve that rises continuously without constraint with increasing pressure, taking the shape of an open S. Theoretical interpretation: It refers to materials that are non-porous or contain very large pores (macropores > 50 nm), such as thick, closed carbon nanotube assemblies. Here, free and unrestricted multilayer adsorption occurs over the open outer surface. (González-García, 2018), (Alharthi et al., 2026)

4.2. ELECTRICAL DOUBLE LAYER CAPACITANCE (EDLC) THEORY

Electrical double layer capacitance (EDLC) theory is the cornerstone of explaining the energy storage mechanism in carbon nanotubes, particularly in supercapacitors. The basic principle of the theory is that, unlike conventional batteries which rely on chemical reactions (oxidation and reduction), EDLC theory relies on a purely physical mechanism for charge storage. When an electric potential is applied to a carbon nanotube immersed in an electrolyte solution, electrons accumulate on the carbon surface. In response, oppositely charged ions in the solution are attracted and align on the electrode surface. This static attraction leads to the formation of two distinct layers of charge (a layer on the carbon surface and a layer of ions) separated by a very small nanometer-sized distance, known as a "double layer." (Chen et al., 2024)

The electrical capacitance of the double layer (C) is calculated using the following equation:

$$C = \frac{\varepsilon_r \varepsilon_0 A}{d}$$

ε_r: Dielectric constant of the solution.

ε_0: Permissibility of vacuum.

A: Accessible surface area of the electrode.

d: Distance between the electrode surface and the ion center (double layer thickness).

From the above equation, the close link between EDLC theory and BET analysis becomes clear. The area effect (A) demonstrates that the relationship between capacitance and surface area is directly proportional. Therefore, materials with enormous surface areas, as measured by BET (such as graphene and carbon nanotubes), theoretically exhibit the highest energy storage values. But here's the thing—new research points out that getting the best performance isn't just about cranking up the surface area. It takes a smart approach to designing the pores themselves (Zhou et al., 2025). When it comes to pore size, ions need pores that actually match their own solvated diameters; otherwise, they just can't get in and do their job within the EDLC structure. Sure, super small pores—micropores under 2nm—can make the BET surface area look impressive on paper, but they often end up blocking or trapping larger ions. On the flip side, medium-sized mesopores (2-50nm) make things a lot easier. They let ions move freely, cut down on resistance inside the system, and help the double layer store charge more efficiently. (Chen et al., 2024), (Zhou et al., 2025)

4.3. CHARGE TRANSPORT KINETICS

Charge transport kinetics is really at the heart of understanding how electrons and ions travel through carbon nanoelectrodes when you charge or discharge them. BET theory tells you how much space is available, and EDLC theory shows you how storage actually happens—but charge transport kinetics reveals how fast and efficiently everything works.

If you want to judge how well carbon nanoelectrodes perform, you can't just look at how much charge they store. You need to pay close attention to the kinetics, since that's what controls how electrons move through the carbon structure, and how they keep pace with ions as they weave through the electrolyte and the tiny nanopores. (Liu et al., 2024).

This kinetics is subject to two main types of dynamic resistance: intrinsic electronic resistance, which relates to the ease with which electrons flow within the carbon crystal structure. Thanks to the sp^2 hybridization of carbon in graphene and carbon nanotubes, these materials possess superior electrical conductivity, enabling rapid ballistic electron transport and reducing contact resistance and electrode intrinsic resistance (Liu et al., 2024). Ionic diffusion resistance, on the other hand, is governed by Vic's Second Law. This resistance describes the kinetics of ion transport from the depths of the electrolyte solution into the pores of the carbon nanotubes.

Here, the close and dynamic relationship between charge transport kinetics and the previously mentioned BET analysis and pore structure becomes

apparent. Materials with a large surface area resulting solely from very fine micropores suffer from extremely slow charge transport kinetics and energy loss due to high hydroelectric resistance and narrow nanochannels (Roberts et al., 2025). In contrast, the presence of a hierarchical pore structure that combines mesopores as fast transport channels and micropores as storage sites ensures a reduction in the diffusion path length, which significantly increases the electrode's efficiency when operating under high current rates (Roberts et al., 2025).

CONCLUSION

Carbon nanotube electrodes are a game-changer for drug analysis. They handle all sorts of molecules and concentrations without breaking a sweat, which puts them at the heart of efficient, portable biosensors—whether that's for testing drugs, solving forensic puzzles, or checking for pollutants.

If we want these modified carbon paste electrodes to move out of the lab and into real-world diagnostics and quality control, here's where the research needs to go:
1. Microfluidic and Lab-on-a-Chip Integration: The next step is to shrink these electrodes down and build them into screen-printed arrays that fit onto microfluidic lab-on-a-chip systems. This way, you get continuous, automated testing—perfect for clinics or even out in the field.

2. Chemometric & AI-Driven Multi-Component Deconvolution: Pairing advanced pulse voltammetry with artificial neural networks and principal component analysis is the way to go. This combo can untangle even heavily overlapping voltammetric signals in complicated drug mixes and messy biological samples.
3. Sustainable & Green Nanotechnology Architectures: Research needs to head in a greener direction—think modifications with eco-friendly nanoparticles, natural biopolymers like functionalized chitosan, and safe ionic liquids. This keeps everything in line with Green Analytical Chemistry principles and makes the tech more sustainable.

4. In Vivo Diagnostic Platforms & Wearable Sensors: When you glue these high-tech carbon nanotube materials onto flexible, biocompatible polymers, you open the door for non-invasive, wearable sensors. Real-time drug monitoring? Transdermal patches for tracking medicine in the body? These aren't pipe dreams—they're right on the horizon.

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