

APPLICATIONS OF CARBON NANOTUBES IN CHROMATOGRAPHY

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Abstract: Carbon nanotubes (CNTs) are cylindrical allotropes of carbon. They were discovered in the year 1991 and they have a unique structure. Due to the huge production and applications of carbon nanotubes, they have attracted many industries and companies towards themselves as they are used in nanotechnology, membranes, capacitors, polymers, metallic surfaces, ceramics, nanomedicine etc. The main motive of this paper is to highlight the basic adsorption capacity of the Carbon nanotubes, and it also reveals that the thermal and chemical stability make them suitable materials as new stationary phases and pseudostationary phases. And also for adsorbents in solid-phase extraction (SPE) and solid-phase microextraction (SPME). This article describes the latest applications of Carbon nanotubes (CNTs) in chromatography.

Keywords: Carbon nanotubes, Chromatography, Stationary phase, Membranes, Extraction

I. INTRODUCTION

Carbon nanotubes (CNTs) were formally discovered by Sumio Iijima in 1991 when an arc discharge method, previously used to synthesize fullerenes, formed needle-like structures on the negative electrode [1]. Microscopy studies have revealed concentric tubes formed by two to 50 graphene sheets and these structures have been called multi-walled carbon nanotubes (MWCNTs). A few years later, researchers discovered that on the addition of iron (Fe) or cobalt (Co) to one of the electrodes single graphite tubes known as single-walled carbon nanotubes (SWCNTs) were formed [2]

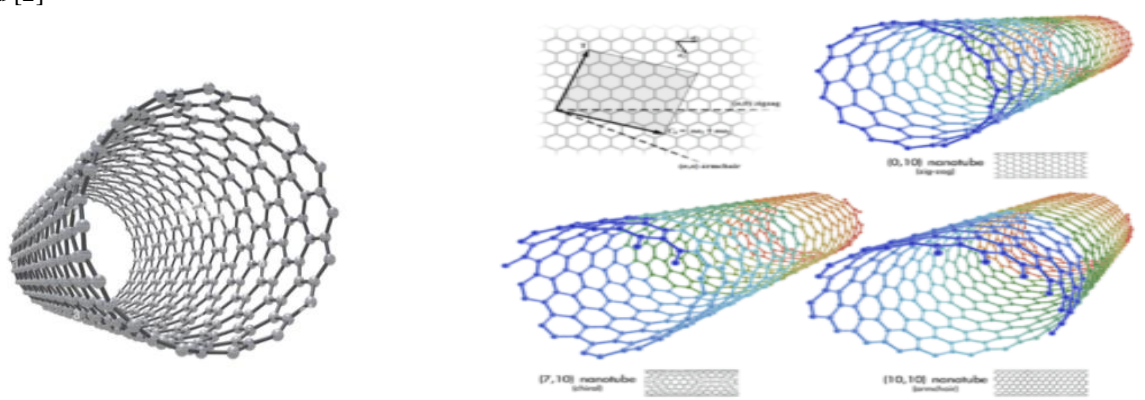


Figure: 1 Carbon Nanotubes

The controlled and exact synthesis of SWCNTs and MWCNTs in comparatively high amounts is possible via techniques such as arc-discharge [4], laser ablation [5], or chemical vapor deposition (CVD) [6]. These processes are, in general, difficult and expensive even before taking purification into account. Cost-effective methods to produce CNTs in large volumes are still needed.

However, the unique properties of CNTs make them potentially very useful in practice. The tensile strength and elastic modulus of CNTs makes them the strongest and hardest materials known because of the sp² covalent bonds between carbon atoms. But these two properties are only part of their appeal. In general, they show other unique physical, chemical, thermal, and mechanical properties that make them useful for an extensive range of applications, primarily in electronics and electrochemistry. In gene therapy, drug delivery, neuron engineering, biosensor technology, and in biomedical and tissue engineering and in some other fields these are being used. Consequently, CNTs are probably one of the most studied nanostructured materials [7].

CNTs are also playing a significant role in analytical chemistry (Figure 2). This short review attempts to summarize the most important applications relevant to chromatographers.

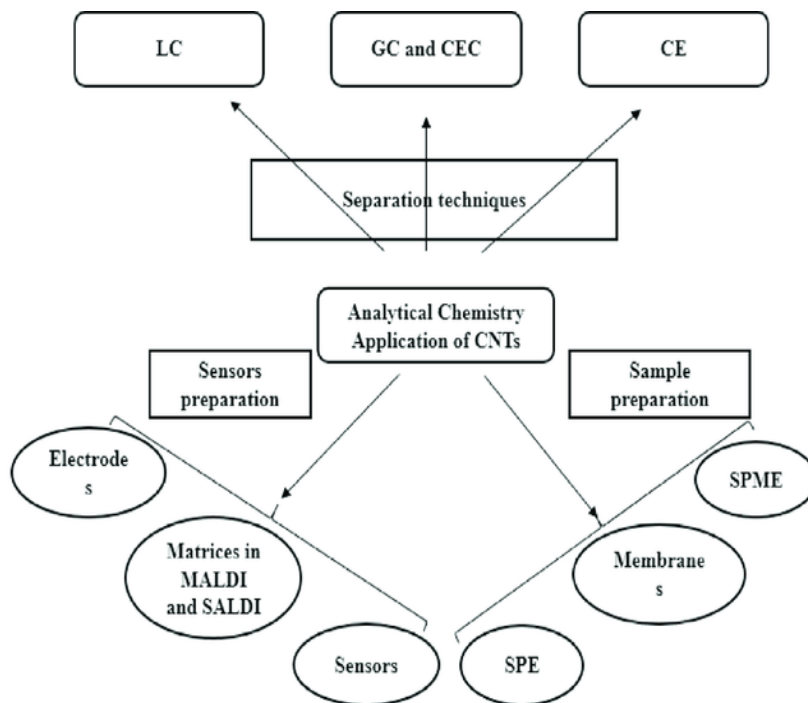


Figure 2: Principal applications of CNTs in analytical chemistry.

Unique Properties of CNTs: SWCNTs along with MWCNTs have a restricted physical, chemical, thermal and mechanical properties. The surface of CNTs can also be easily covalently or non-covalently modified to change their properties. This is useful because many of their desired properties can be preserved, while improving their solubility. Both pristine and modified CNTs have proven to be useful in analytical sciences [8–12] due to the excellent sorption capacity, and great thermal and chemical stability of CNTs. These properties make them potentially useful as stationary phases in gas chromatography (GC), liquid chromatography (LC) and capillary electrochromatography (CEC), as well as pseudo-stationary phases in capillary electrophoresis (CE) [8,9]. Additionally, as a result of their sorption capacity — combined with their cave structure and ability to form a wide range of interactions with foreign molecules — they could also supportive stationary phases for sorption extraction techniques, for example, solid-phase extraction (SPE), as well as solid phase micro extraction (SPME) [13,14]. CNTs have also been suggested as substrates for matrix-supported or surface-supported laser desorption ionization-time-of-light mass spectrometry (MALDI or SALDI-TOF-MS) [15], and also for the production of polymeric membranes for filtration due to the presence of cores and their ability to allow fluids to pass through them [11].

The electrical properties of CNTs, such as conductivity, dielectric constant, impedance and refractive index, mean that they are sensitive to interaction with analytes, or even with complex biological molecules [8]. This is the foundation of their use as gas sensors [16] and biosensors [17]. CNTs also have large active- surface electro catalytic properties- and good electron transfer to -nanoelectrodes.

In this respect, numerous applications describe their use as electrode materials or as modifiers of conventional working electrodes in analytical voltammetry [18]. They have also found a place in anodic strip voltammetry due to the combination of electrical properties and the high sorption capacity [19], and as materials to build and, improve electrochemical detectors- used in microchip/ CE [20].

It is important to emphasize that one of the main challenges of using CNTs in analytical chemistry is to obtain pure and well-characterized materials [21]. However, commercially available CNTs consist of a distribution of nanotubes of different diameters and lengths depending on the manufacturer, which clearly affects their properties and behavior. For this reason, the selection of the type, dimensions, and producer of CNTs must be carefully chosen to ensure the successful transfer of methods developed between laboratories.

CNTs in Separation Techniques: Chromatographic and electro Chromatographic applications: Due to their intrinsic properties, excellent absorbency, and thermal and chemical stability, CNTs have been proposed as stationary phases for GC. Non-functionalized pure CNTs are stable up to 1200 °C under inert atmosphere, which prevents column bleeding and enables operation at higher temperatures than conventional columns [22]. To produce these GC columns, a thin layer of CNTs is deposited on their surface by CVD (9) producing a homogeneous surface with a small number of polar groups that allows a better peak shape. The possibility of functionalizing the CNTs surface inside the column to improve selectivity has recently been investigated; however, it should be noted that thermal stability must be carefully considered because impurities and functionalization directly affect column reliability [23]. Specifically, the infectivity of a high amount of metal- coming from the synthesis of the CNTs- can affect their retention performance. However, the number of applications in this field is still low, and concerns mainly the separation of standard mixtures of volatile compounds such as alkanes, aromatic compounds, esters, and ketones.

The use of CNTs as stationary phases in LC is even less investigated [9,24]. They have mainly been used in combination with a second packing material (normally silica) or incorporated in a porous polymeric monolith [11]. In nearly all of these works, large columns of 4.6 mm of internal diameter have been used. Figure 3 shows the chromatograms of 11 -acidic, neutral and alkaline organic- compounds on PS-DVB-CNT- columns containing, 0%, 1% and 5% MWCNTs. It should be noted that the resolution and plate number both reduced with superabundant MWCNTs in this specific case [25]. Although the applications in this field have increased recently, only test mixtures of analytes have been used in the majority of these works; complex methodologies for real sample analysis have not been developed.

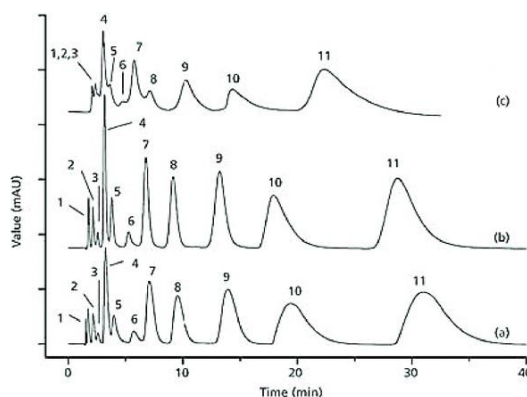


Figure 3: Separation of 11 organic compounds on (a) PS-DVB column, (b) PS-DVB-CNT columns (1% MWCNTs), and (c) PS-DVB-CNT column (5% MWCNTs). Column: PS-DVB and PS-DVB-CNT particles packed in a 150 mm Å—4.6 mm stainless steel column. Mobile phase: methanol/water (90:10, v/v). Detection: UV absorbance at 254 nm. Flow rate: 1.0 mL/min. Peak identification: 1 = resorcinol, 2 = sulfadimidine, 3 = benzylalcohol, 4 = aniline, 5 = p-toluidine, 6 = 2-naphthol, 7 = p-methoxybenzaldehyde, 8 = anisole, 9 = N,N-dimethylaniline, 10 = 1,3,5-trimethylbenzene, 11 = 2-methoxynaphthalene.

CNTs can be covalently or noncovalently paralyzed on the walls of silica capillaries to perform open- tubular CEC(OT-CEC) to determine different composites [11]. In one example, CNTs were incorporated into porous polymer monolithic capillary columns to improve the separation of small molecules [26]. To the best of our knowledge, CEC with CNT-wrapped capillaries has not been developed until now. It is also important to mention that there have been applications with CNTs in chips to perform chip CEC for the determination of alkanes, thioamides, DNA fragments and dyes [11]. In general, few works have been reported so far in the chromatographic and electro chromatographic fields, but the number of papers published in the future is likely to increase due to the interesting results produced by CNTs.

Electrophoretic operations: The use of CNTs in CE lies in their addition to the background electrolytes(BGEs) as pseudostationary phases for the development of electrokinetic chromatography(EKC)(22). Still, because raw CNTs aren't answerable in waterless buffers or common detergents, they're generally covalently or noncovalently functionalized to form stable dormancies. In this regard, both MWCNTs and SWCNTs have been oxidized, mixed with surfactants, ionic liquids, or even dispersed in a microemulsion (aqueous solutions containing dispersed nanometer-sized droplets of an immiscible liquid surrounded by a surfactant to reduce the surface tension between the two liquid layers, e.g. in different matrices, and nucleotides in an extract of chicken [11]. Although several strategies have been espoused to ameliorate solubility of CNTs in the BGE, it's worth mentioning that it is delicate to gain accurate and reproducible attention of the CNTs in the BGE.

II. CNTs IN SAMPLE PREPARATION

Solid phase extraction: From a detailed review of the current literature, one can conclude that CNTs offer a sufficient sorption capacity for the extraction of both organic and inorganic compounds. In addition, the change in selectivity introduced by the covalent or non-covalent functionalization of their face has favored their expansive use in this field [11,13,14,27]. On the one hand, it is believed that the interaction of CNTs with metal ions occurs due to the presence of functional groups in the surface of the material [28] and, as a whole, the metal removal ability of CNTs is enhanced by the presence of active sites on their surface, the inner cavities and inter-nanotube space. In addition, the effect of pH is crucial and should be carefully studied. The existence of a pH value called "point of zero charge" [29] or "isoelectric point" (at which the electric charge density on the CNT's surface is zero) causes the surface of CNTs to become negatively charged at a pH higher than this. It improves the adsorption of cationic species.

On the negative, when the pH is lower than this value, protons contend with essence cations for the same spots on the face of CNTs. Precisely for this reason, solutions containing acidic additives are frequently used to promote the elution of metals.

A number of approaches for metal ion extraction have focused on the use of oxidized CNTs (o-MWCNTs or o-SWCNTs), obtained by subjecting CNTs to a strongly acidic media at high temperatures. These conditions introduce $-COOH$, $-OH$, and $-CO-$ groups, after which different substitution reactions can be carried out. In this way, organic species or even biomolecules are also immobilized on their surface to expand their application [14,27]. Complexation of essence ions may not be necessary when using modified CNTs, in discrepancy to what's demanded when CNTs are not modified (as is generally the case with other sorbent accoutrements). In this field, the vast maturity of workshop have been developed to prize inorganic analytes from waterless samples, and only a many reports have dealt with solid or semi-solid matrices [11,13,27].

The strong sorptive interaction of organic analytes has been attributed to $\pi-\pi$ electron donor-acceptor relationships between the aromatic system of organic molecules (electron acceptors) and the highly polarizable graphene sheets of CNTs (electron donors) [8]. For this reason, a number of authors have worked with non-modified CNTs in this regard, substantially to prize fungicides [13,30], but also other substances similar as PAHs, parabens, antioxidants, medicinals, phthalate esters, phenolic and natural composites [11,13].

Conversely, retention of polar organic analytes has been described as more efficient with functionalized or modified CNTs. This is because the commerce between functional groups or paralyzed organic moieties on the face of CNTs is more selective. In this respect, o-CNTs have been successfully assessed, together with magnetic CNTs (m-CNTs) [31,32], which are formed by the assembly of magnetic nanoparticles on CNTs through chemical/physical modifications. Figure 4 shows the scanning electron microscopy (SEM) images of Fe/MWCNTs mixes with different original mass rate of ferrocene to CNTs [33]. Magnetic CNTs have facilitated the manipulation of CNTs in dSPE as they can be manipulated with an external magnetic field provided by a strong magnet.

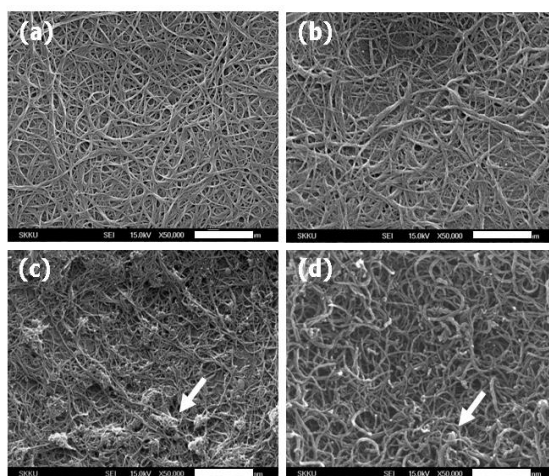


Figure 4: SEM images of (a) pristine MWCNTs and Fe/MWCNTs composites with an initial mass ratio of ferrocene to CNTs of (b) 1:1, (c) 2:1, and (d) 3:1. Adapted from reference (33).

Organic molecule-modified-CNTs have been described for certain applications, and the introduction of molecularly imprinted polymers (MIPs) on the surface of CNTs has also been exploited as one of the most selective ways to perform SPE, although multi-residue analysis cannot often be undertaken due to the high specificity of the template molecule. Similar to inorganic analytes, CNTs have mainly been used to extract organic compounds from various types of water, but also in various complex matrices (milk, oil, honey, eggs, fish, meat, cosmetics), soil have also been analyzed [11,13,27].

CNTs with different dimensions, number of walls or type of functionalization were compared. CNT Performance Compared to Other Types of Stationary Phases B. C18, Activated Carbon, Graphite Carbon black (GCB) and polymeric adsorbents have also been investigated. In most cases, CNTs showed higher sorption capacity or, at least, similar efficiency. Regarding the amount of CNTs required for extraction, it is very common to use between 30 mg and 100 mg, even for the extraction of high volumes of liquid samples or extracts [11].

Finally, and like other SPE sorbents, CNTs have been part of studies regarding automated and miniaturized procedures. Automation also means some miniaturization due to the use of SPE mini-columns. However, in the case of CNTs and due to their dimension and structure, they tend to create flow resistance when used as mini-column packing material, with a risk of channeling. For this reason, the use of alternative μ -SPE systems by packing CNTs inside porous materials offered a good alternative to μ -SPE using mini-columns [11]. Solid phase microextraction: The most difficult challenge in CNT-SPME is finding a suitable, reproducible and convenient procedure. Permanent coating process.

Different methods have been used to deposit CNTs in SPME fibers, including sol-gel technology, chemical bonding, electrochemical polymerization, electrophoretic deposition, physical agglutinating by an organic binder, atom transfer radical polymerization, and magnetron sputtering [34,35]. Traditionally, fused silica has been used as a suitable fiber material due to the presence of silanol groups on the surface. However, the brittle fused silica fibers are replaced by metallic fibers, such as stainless steel wires, to solve this important problem.

In general, sol-gel technology has been used the most, but its insufficient reproducibility has given way to other methods, such as simpler chemical bonding methods [35]. Electrochemical polymerization can also be an alternative, but the lack of bonding between the coating and the substrate generates fibers with low thermal stability and swelling in organic solvents. Similarly, electrophoretic deposition has emerged as an alternative to fabricate stiffer and more stable CNT-SPME fibers. However, until now, a limited number of researchers have used these methods to coat the SPME fibers with CNTs [11,13,35]. Physical agglutination with glue also provides fibers with low stability and resistance, with the added inconvenience that glue can block the coating pores or even alter extraction selectivity.

As in SPE, the selectivity of the CNTs can be modified by introducing functional groups on their surface for the determination of polar compounds. For this reason, both modified and untreated CNTs (MWCNTs and SWCNTs) have been used as SPME coatings for the extraction of organic analytes such as many pesticides, phenols, and pharmaceuticals [11,35], and to a lesser extent for the extraction of inorganic trace ions [11].

Normally, home-made CNTs fibers were compared with commercially available fibers to evaluate their performance in terms of extraction efficiency and durability. In most publications, CNT fibers showed higher sensitivity and selectivity and higher or comparable extraction efficiency. It also improves thermal and physical resistance.

Membranes: Traditional polymeric membranes used for water purification and gas separation suffer from several problems: low selectivity, permeability and susceptibility to obstruction or fouling. CNTs have been used to solve some of these drawbacks and most manuscripts have focused on the use of different types of membranes with CNTs embedded in a polymer matrix. Although this type of membrane offers high stability and efficiency, low cost and ease of operation, its manufacture is still under development to prevent aggregation. However, some of them have already been used successfully for different applications [11].

III. OTHER APPLICATIONS

Electrodes: There are numerous applications in the literature based on the application of CNTs as electrode materials or modifiers of conventional working electrodes [8,18,36]. Their use is justified by their important advantages in electrochemical measurements such as the large active surface at electrodes of small dimensions, the improved electron transfer or the often indicated electrocatalytic properties. Analytical methods based on voltammetric stripping techniques also benefit from the unique properties of these electrodes: B. Stronger adsorption of many organic compounds, resulting in much lower potential for stripping reactions and improved electroanalytical signals.

Electrochemical detectors: The excellent electroanalytical properties of CNTs-modified electrodes have favored their use as electrochemical detection systems coupled to separation techniques because they improve the determination of certain compounds [37]. In addition, nanoelectrodes and nanoelectrode arrays composed of CNTs can be integrated with microelectronics and microfluidic chips, a fact that expands their application in this field.

Gas sensors and biosensors: The use of CNTs in gas sensors is based on changes in the electrical properties (conductivity, permittivity, impedance, refractive index) of these materials caused by charge transfer with gas molecules [8,38]. In this way, changes in the resistance of the CNT layer (and therefore in the impedance) were exploited for the detection of polar (NH₃, CO, O₃) and non-polar (He, Ar, N₂, O₂, CO₂) gases [8]. The sorption properties of CNTs have been used in piezoelectric detection of volatile analytes such as alcohols and inorganic gases (He, Ar, O₂, N₂) and in surface acoustic wave sensors to detect volatile organic compounds [8,38]. Also, thermoelectric properties of SWCNTs have been used for the analysis of gases in contact with them [39]. Pristine as well as polymer-modified CNTs have been used to construct gas sensors, which take several hours to release the analyte at room temperature before they can be reused [38].

CNTs have also been used to construct electrochemical biosensors to detect enzymes, genes, immunological proteins, neurotransmitters, and other redox proteins [37,40,41] due to their ability to promote electron transfer in electrochemical reactions. The most advantageous method is to directly attach specific proteins or clinically relevant biomolecules to CNTs. Various types of electrochemical methods have been used in these sensors, including direct electrochemical detection using amperometry and voltammetry, indirect detection of oxidation products using enzymatic sensors, and conductivity change detection using CNT field effect transistors. The electron transfer in the detection process can be made directly in the CNTs, in CNTs-polymer composites, in CNTs-metal nanoparticles, and in other CNTs composites (including biological composites).

Matrices in laser desorption–ionization: The use of CNTs as matrices in laser desorption–ionization overcomes some of the disadvantages that exist when molecules with masses lower than 500 Da are analyzed by these methods. Most of the organic matrices are decomposed into low mass interferences that generate a high matrix background that hinders mass spectra interpretation [42]. The high surface area of CNTs allows for good analyte dispersion, preventing sample aggregation and strong UV laser absorption. Nevertheless, contamination of the source by CNTs flying away from the target has been described and therefore some caution should be taken. To avoid this, an adhesive can be added to hold the particles to the stainless steel plate. In the few existing applications in this field, different molecules have been analyzed, including peptides, carbohydrates, amino acids, pyrenes, low-fatty chains, and other low-mass biomolecules [11].

IV. CONCLUSIONS

The combination of structures, dimensions and topologies make CNTs interesting alternative materials, and therefore research for their applications in separation science will increase.

CNTs as stationary phases in GC and LC and as pseudostationary phases in CE are receiving more attention; however, they have modest potential at the moment. Conversely, their growth in sample preparation applications, especially in SPE, has increased significantly, with a large number of works published in this area.

The main drawback is that CNTs may contain some impurities from the synthesis procedure that interfere with the ulterior analysis, but this is something that can be easily resolved by acid treatment or solvent washing.

The facile functionalization, attachment of complex foreign molecules, and the potential for solubilization make CNTs very exciting and powerful materials. This greatly expands their application in analytical chemistry and further research in this regard is expected to increase.

Although a wide variety of highly pure CNTs are already commercially available, they are relatively expensive. This is probably due to their low demand and the low yields obtained in the synthesis steps. However, a reduction in prices is expected when these materials are used more widely, especially in sample preparation. CNTs have a rich and unique history with much potential for the future.

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