Nanoparticles as stationary and pseudo-stationary phases in chromatographic and electrochromatographic separations

Ai-Hong Duan, Sheng-Ming Xie, Li-Ming Yuan

To improve selectivity, chemical stability, and separation efficiency of chromatography, many past papers reported on nanoparticles (NPs) being used as stationary phases in chromatography. This article covers applications of NPs, including carbon nanotubes, fullerenes, gold NPs, silica NPs, zirconia NPs, and titanium-oxide NPs, as stationary phases in gas chromatography, high-performance liquid chromatography, capillary electrophoresis and capillary electrochromatography.

We discuss the advantages and the disadvantages of nanomaterials as stationary phases compared to other materials, including traditional stationary phases. We also discuss future possibilities for developing nanomaterial-based stationary phases.

Keywords: Capillary electrochromatography; Capillary electrophoresis; Gas chromatography; High-performance liquid chromatography; Nanomaterial; Nanoparticle; Pseudo-stationary phase; Separation; Stationary phase

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1. Introduction

Nanomaterials with at least one dimension of ~1–100 nm have received much attention due to their novel chemical, physical and electrical properties. Nanoparticles (NPs) include silica NPs (SiNPs), gold NPs (AuNPs), titanium-dioxide NPs (TiO_2NPs), carbon NPs, polymer NPs, molecularly imprinted polymers, molecular micelles, and dendrimers. Nanotechnology has significantly accelerated the development of many fields of science. The applications of NPs are increasing in separation science. They provide unique opportunities for the development of higher performance separation techniques that utilize NPs that possess a large surface-to-volume ratio. There have been several reviews on this topic [1–4].

In 1903, Russian scientist Tswett created the chromatography-separation technology, which has developed into a new discipline since the 1940s. Beginning in the early 1960s, stationary phases, comprising a core substrate with NP spheres arranged in various manners on the surface of the core substrate were being implemented in chromatographic systems. Kirkland reported on superficially porous silica microspheres using a nonporous glass-bead core with nm-sized silica spheres attached to the core. According to the experimental results, compared to the untreated beads, the columns exhibited higher separation efficiency and selectivity due to having more efficient mass transfer of solute.

Chromatography has been widely used for high-resolution separation and quantitative analysis, and became an essential research method and tool of life sciences, materials science, and environmental science. Currently, developments on chromatography technology focus on new stationary phases, detection and methods. Significant progress has been achieved, especially after the introduction of nanomaterials into separation science. An ideal chromatographic stationary phase should possess good chemical stability, selectivity, and separation efficiency in chromatography. The characteristics of four main chromatographic methods are

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Table 1. Comparison of four chromatographic methods

Methods	Advantages	Disadvantages	Nanomaterial-based stationary and pseudo-stationary phases	Ref.
GC	High efficiency	Low resolution for some gases	High resolution for gases; Improving selectivity; Very high temperature resistant	[1]
HPLC	Wide application	–	Enhancing selectivity	[3]
CE	High efficiency	Low resolution for some neutral samples	High resolution for neutral samples; Improving selectivity	[4]
CEC	High efficiency	–	Enhancing selectivity	[2]

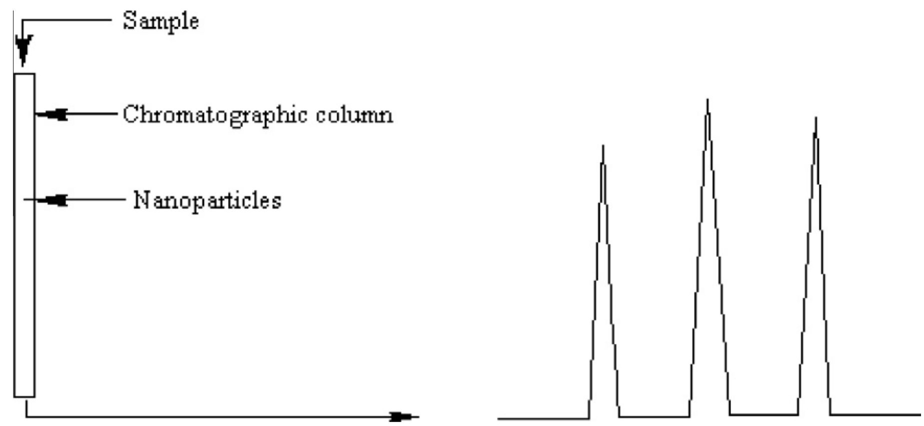

Figure 1. Nanoparticle-based chromatography.

compared in Table 1, and Fig. 1 is a diagram of NP-based chromatography.

As can be seen from Table 1, use of NPs for chromatography has proved to be advantageous. On the basis of current developments, a series of NPs (e.g., SiNPs, carbon NPs, AuNPs and silver NPs) have been used as stationary phases that achieved higher selectivity and separation efficiency in gas chromatography (GC), high-performance liquid chromatography (HPLC), capillary electrophoresis (CE) and capillary electrochromatography (CEC).

This review article focuses on NPs with emphasis upon their application in the stationary phases for chromatographic separations.

2. Gas chromatography

GC has evolved as a powerful analytical tool in the separation and analysis of gases and analytes with low boiling temperatures. Gas-solid chromatography utilizes the sorption of the solute on a solid stationary phase, and partitioning to gas-LC as the dominant mechanism. Non-functionalized and functionalized NPs have been widely used as stationary phases for GC. Some representative examples of the use of NP-based stationary phases are shown in Table 2.

2.1. Carbon nanotubes

A packed column with purified multi-walled carbon nanotubes (MWCNTs) was used in GC and the ability of the column to separate aromatic hydrocarbons, alkanes, halogenated hydrocarbons, alcohols, ketones, esters, and ethers was investigated. The results showed that MWCNTs can be an excellent GC packing material. Compared to graphitized carbon black, MWCNTs showed stronger retention of compounds and more symmetric peaks [5].

CNTs in powder often form large aggregates, because of which much of their nanoscale characteristics may be lost when using CNTs as packing material in GC. A film of CNTs could be deposited by chemical-vapor deposition (CVD) to form the stationary phase in open tubular format [6]. The self-assembled CNTs demonstrate classical chromatography behavior and high resolution. A major advantage of this method is the ease of fabrication by the self-assembly of CNTs directly on the tube surface to obtain a stable stationary phase. At the same time, the thickness of the CNT film and its morphology can be tailor-made by varying the CVD precursor, catalyst preparation and chemical functionalization [7].

Microfabricated GC columns receive considerable attention because of their small size, low power consumption, and low thermal mass. An application of single-walled CNTs (SWCNTs) as the stationary phase in