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The third way in analytical nanoscience and nanotechnology: Involvement of nanotools and nanoanalytes in the same analytical process

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ABSTRACT

The classical working lines of analytical nanoscience and nanotechnology (AN&N) are the characterization/determination of nanomaterials and their use as tools (e.g., sorbents, inert/active supports, and sensors) for improving analytical processes. A widely discussed topic in the context of AN&N consists of the synergistic combination of these two facets in the same analytical process; that is, the determination of nanomaterials using nanoparticles of the same or different nature. This is a promising approach, named as "third way" in AN&N in this study for the first time, which is of great relevance not only in the analytical chemistry realm but also in nanoscience and nanotechnology. In this study, the definition of the "third way," the corresponding objectives and classifications as well as the incipient state of the art of this topic are critically presented. This study also presents examples concerning the determination of nanomaterials using nanoparticles and their classification based on the nanoparticle used as tool (e.g., metallic, carbon, or hybrid nanomaterials). They have been applied for the determination of a variety of nanomaterials in environmental, biological, or food matrices, with the nanotools being involved in different steps of the analysis. The main purpose of this study is to share with the chemical community a new and promising route to extract reliable information from nanoscience and nanotechnology.

Contents

Abbreviations: a-CDs, Amine-derivatized carbon dots; AFM, Atomic force microscopy; AgNPs, Silver nanoparticles; AN&N, Analytical nanoscience and nanotechnology; AuNPs, Gold nanoparticles; CDs, Carbon dots; c-SWNTs, Carboxylic single-walled carbon nanotubes; EDTA, Ethylenediaminetetraacetic acid; EELS, Electron energy loss spectroscopy; GO, Graphene oxide; GQDs, Graphene quantum dots; MWNTs, Multiwalled carbon nanotubes; PAMAM, Poly(aminoamine); PPRs, Polypseudorotaxanes; QDs, Quantum dots; SERS, Surface-enhanced Raman scattering; SWNTs, Single-walled carbon nanotubes.

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1. Introduction

Recently, nanoscience and nanotechnology has become a widely discussed scientific and industrial topic that has and will have an influence on technology and on quality of life of the individuals using nanotechnology-based products. Consequently, *the requirements of information* and the number of scientific papers on this emergent area grow exponentially, so also the nanoproducts introduced in the market and the nanoparticles and/or nanostructured materials in the environment. These requirements of information emerge from the need for monitorization/control of raw, intermediate, and final products and residual wastes in the realm of industry (e.g., manufactured nanofood [1,2]). In addition, nanotoxicology studies [3] need reliable information to establish clear rules to protect humans, animals, and plants from these new pollutants.

On the contrary, the unique physicochemical properties of nanomaterials are exploited to develop, among others, excellent nanosensors to provide *information* on a variety of objects/systems that support the development in a variety of areas (e.g., nanomedicine [4,5]).

The following is a framework of the topic under study. First, the classical relationships between nanoscience and nanotechnology and analytical chemistry are described. On the contrary, the so-called "*third way*" is defined, and its objectives and types are described in the following sections. Then, relevant examples of analytical nanoscience and nanotechnology (AN&N) involving nanomaterials both as tools and analytes in the same analytical process are described. This study, not being an exhaustive review, shows the application potential of nanostructured materials.

2. The two classical facets of AN&N

On the basis of the role played by nanomaterials, nanoscience and nanotechnology and analytical chemistry have two types of relationships (Fig. 1):

(A) Nanomaterials can be characterized and/or determined in a variety of samples, such as cosmetics, agrifoods, and clinical and environmental matrices. The valuable (bio)chemical information of analytical chemistry provides a significant support to the integral development of nanoscience and nanotechnology. Despite its strategic importance, the number of analytical studies on nanoscience and nanotechnology only accounts for 30–35%. No doubt, analysis (both characterization and determination) of nanomatter should be enforced.

(B) Nanomaterials can play different roles (sorbents, stationary and pseudo-stationary phases, inert and active supports, fluorophore probes, and electric conductors) to improve the existing and develop new analytical processes, aiming to exploit the unique physicochemical properties of the nanomatter, thereby enhancing the analytical properties, which are indicators of the quality of the information provided. About 65–70% of the articles published in AN&N are related to the use of nanomaterials as analytical tools.

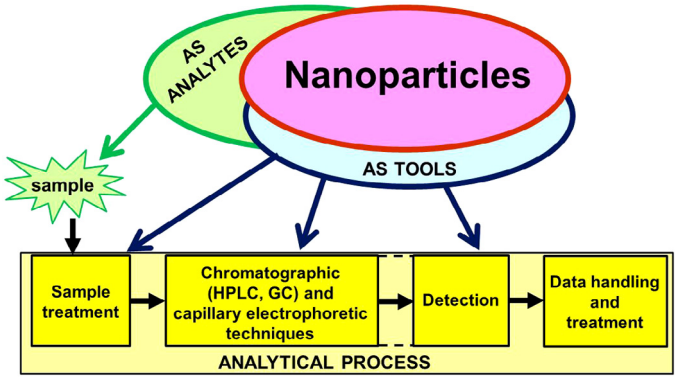

Fig. 1. The two classical facets of analytical nanoscience and nanotechnology according to the role played by the nanoparticles in the analytical process: as analytes or tools.

3. The third way in AN&N

3.1. Definition, objectives, and types

The so-called "*third way*" serves as a complementary alternative to the two classical facets of AN&N. The description, objectives, and types of this approach are outlined in this study.

Fig. 2 depicts the concept of the third way as a combination of the two classical facets (A and B) described previously. Nanoparticles or nanostructured matter can simultaneously act as an object (analyte) in the sample and a tool in different steps (sample preparation, chromatographic or capillary electrophoresis separation, and detection) of the same analytical process. Despite its strategic importance, only few articles have been published in this topic so far.

The primary aim of the "*third way*" is to improve the existing and develop new and promising approaches to extract chemical information from nanoscience and nanotechnology. This objective is supported by the following facts: 1) The need for appropriate tools to enforce the characterization and determination of nanomaterials; 2) The increase of engineered nanomaterials that propitiate the increase of new analytical (informative) problems to be solved; and 3) The current low added value of reputed journals of classical papers (e.g., use of carbon nanotubes (CNTs) as sorbents in solid-phase extraction). Another supporting factor for the aforementioned objective is the investigation of synergies between the unique properties of nanoparticles or nanostructured matter that can act as analytes and tools, that is, the interaction between them in the same analytical process enhances the top (accuracy and recovery), basic (precision, sensibility, and selectivity), and productive (rapidity, costs, and risks) analytical properties.

There are several types of analytical processes than can be considered in the framework of the "*third way*." Using different criteria, five noncontradictory but complementary classifications can be found (Fig. 3). The *first classification* considers the difference between

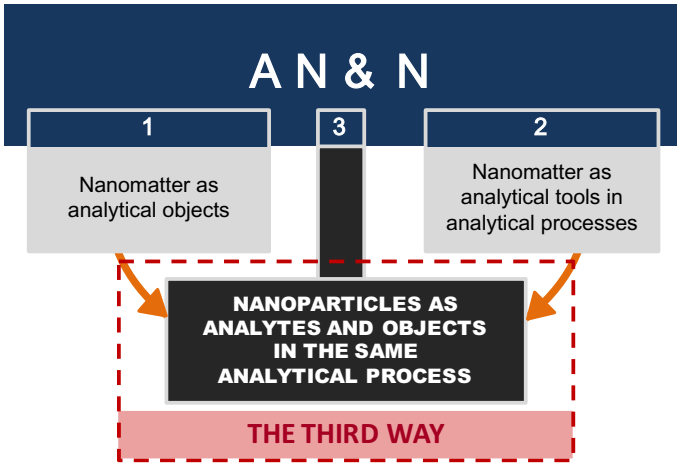

Fig. 2. Schematic representation of the two classical facets of analytical nanoscience and nanotechnology (1 and 2) and their combination in the so-called third way (3), which implies the involvement of nanoparticles, of the same or different nature, both as tools and objects (analytes) in the same analytical process.