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EDITORIAL

Nanoanalytics: analytical methods for characterization of nano- and micro-objects

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This special issue is devoted to analytical chemistry whose analytical targets are objects with sizes smaller than a few micrometers. Interest in such objects finds its roots in the history of human society. As John T Stock wrote in 1977, the consideration of the past knowledge enables the "risk of presenting a distorted perspective of science" to be minimized and "guidelines for the future" to be given (Stock 1977). Therefore, a brief history of chemistry, analysis, and analytical chemistry introduces the subject of this special issue.

Chemistry and analytical chemistry Since the beginning of humanity, Man has sought to understand matter to use it. Man also intuited that matter was a combination of indestructible basic elements, that the Greeks were the first to name atoms (Karayannis and Eftathiou, 2012). Until the nineteenth century, chemical analysis was considered as a way for the experimental development of chemistry. Then, many conceptual and methodological advances were made. This enabled chemical analysis to be seen as a system of knowledge, and analytical chemistry to emerge as a branch of Science (Niinistö 1993; Vershinin et Zotolov, 2009). Modern analytical chemistry has its deep roots in the twentieth century, where instrumentation and methods for acquisition and processing of acquired information were developed. At the end of the twentieth century, these developments, together with the emergence of new analytical targets, both elements and molecules, led to a profound evolution, even revolution in analytical chemistry, in theoretical, conceptual, and methodological terms. Analytical chemistry has also specialized, giving birth to disciplines each with its own theories and concepts, such as speciation, isotopy, or omics.

On the "nano-road" The sophistication of the techniques, tools, and know-how on which the industrial age is based has increased exponentially over the last century, due to advances in scientific knowledge. With the advent of technology, another revolution occurred in the post–second World War: the miniaturization of tools. This began with the development of microelectronics: the first integrated circuits, the "chips," were designed on silicon support of a few millimeters. Miniaturization has proved very interesting economically and technically, the chips being inexpensive, capable of integrating several functionalities, and enabling fast operation. The mass production of miniaturized systems thus opened the way to many applications. For that, the top-down miniaturization route was used, i.e., that smaller and smaller structures were manufactured from macroscopic materials. However, this approach revealed physical limitations because quantum phenomena appearing at small dimensions were poorly controlled. One solution was to use a bottom-up approach. The idea was to assemble the basic bricks of matter, i.e., to manipulate the matter atom by atom to build the desired object. This approach would enable quantum phenomena to be well controlled. This could also help to further reduce manufacturing costs. This was achieved from the 1980s: synthesizing objects smaller than a micrometer. These objects could then be manipulated according to the needs, for example, associating particles with other particles or with molecules to acquire the desired functionalities, be kept in suspension, or be placed on supports or in solid matrices. The first syntheses of submicron objects were also possible because of the development of observation techniques adapted to the atomic and (sub)nanometric scales. Especially electron microscopy techniques enabled the synthesized nanoparticles to be visualized, and thus to be characterized individually.

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Miniaturization has proven to provide advantages in many other fields besides electronics: optics, fluidics, mechanics, chemistry, biochemistry, medicine, etc. Thus, the miniaturization revolution led to the development of the following:

1. Research to understand the physical, chemical, and biological properties of nano-objects as well as their manufacture and assembly. The corresponding activities have been grouped under the term nanosciences, at the crossroads of founding disciplines, physics, chemistry and biology, and many others.
2. Tools, techniques, and know-how to synthesize and use nanometric structures and/or objects. All of these achievements have been identified as nanotechnologies. Their current and potential applications are in all sectors: pharmaceutical, medicine, environment, food, analysis, energy, transport, etc.

Nanosciences, analytical chemistry, and nanoanalytics The term "nanoparticle" appeared in the scientific literature with the meaning we give it today in the late 1970s. A dozen articles were devoted to nanoparticles until 1980. The number of studies on this subject exploded in the following decades: Compared to 1971–1980, 15 times more in 1981–1990, 700 to 1000 times more in 2005–2014; and almost as many works in the last 4 years as in the previous 10 years. Over the last 40 years, most of the work on nanoparticles has been devoted to their biological effects and their use for medical purposes. However, over time, the environmental fate of nanoparticles and colloidal particles has become increasingly important in all published studies. While characterization of nanoparticles was addressed in 20 to 30% of the work, the methodological aspects related to the characterization of nanometric objects and micrometric aggregates were the main focus in only about 10% of the studies. It is interesting to note that the characterization issue was addressed in most work on the environment.

From these few figures, it appears that the place of analytical chemistry within nanosciences remains an open question. Karayannis and Eftathiou (2012) addressed this point a few years ago. They wrote, "Analytical chemistry is an ancient art and its tools and basic applications date back to the recorded history. (…) Nanotechnology is today an area, which gives new dimensions to analytical chemistry." These authors also consider analytical chemistry as "the key to solve problems related to material systems and to society." However, in most cases, nanotechnologies appear as serving the tools of analytical chemistry: For example, carbon nanotubes were used as adsorbents in stationary chromatographic phases, nanomaterials applied the determination of biomolecules, or nanoparticles used for the bioelectronic detection of biomolecules (Karayannis and Eftathiou 2012). Analytical chemistry is very interested in the effects of nanoparticles on the medium in which they are found, and on the constituents of this medium, elements, molecules, or living organisms, which are then the targets of the chemical and biological studies. But do we really know what nanoparticles are introduced or generated in the medium studied? What about the effects of this medium and its components on nanoparticles?

Today, the bottom-up approach strongly stimulates the development of nanosciences and nanotechnologies. This approach necessarily makes the characterization of nano-sized objects a central issue. Their structure, their nature, and all the properties that result from them also induce many analytical questions. Other issues are inevitably associated, among which are the following:

1. Which descriptors of nanoparticles should be determined? This question is associated with that relating to the link between these descriptors and the context of the study. For example, the impact of nanoparticles on their environment (including living organisms) should be seen interdependently and the observed state of the system studied the consequence of synergistic effects. The question of the constituent and/or associated elements with the nanoparticles is particularly important when these elements may have their own effects; fate of elements should then be associated with the knowledge of physical and chemical speciation;
2. How to proceed methodologically? In other words, what characterization strategies should be developed knowing that, from the singular nature of nanoparticles, new issues relating to the traceability and validation of these strategies arise?

Obviously, there is still much to be done in terms of analytical chemistry. The first one is to consider objects of nanometric size as analytical targets in their own right, that is to say as objects of study for which it is necessary to understand the physical, chemical, and analytical singularities to understand the incidences on their observation and study.

The nanoanalytics session of the Euroanalysis 2015 conference held in Bordeaux, France, was organized to promote exchanges on these issues, and in particular:

1. position analytical chemistry within the nanosciences,
2. see what legitimizes the emergence of a new discipline within analytical chemistry, i.e., nanoanalytics,
3. illustrate the issues and applications of this discipline,
4. promote and disseminate knowledge about this discipline and its applications.

These different points were discussed during the oral presentations and associated debates. This special issue presents some points of reflection on the scientific exchanges that took place during this conference. It also focuses, through application studies, on some methodological aspects of characterization, such as speciation, multi-method, and/or multi-technique approaches, couplings, openness to other sciences such as computational chemistry. Since environmental sciences are often driving analytical development especially in the field of materials and particles, the application studies illustrating this special issue concern environmental applications.

Analytical chemistry is a scientific discipline open to others. It is the same for nanoanalytics, which is fundamentally interdisciplinary. John T Stock wrote in 1977 that large areas of analytical chemistry remain open to exploration. This statement is still true, as evidenced by this special issue.

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