



Review

Recent trends in nanomaterial-based microanalytical systems for the speciation of trace elements: A critical review



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HIGHLIGHTS

- First critical review comparing different nanomaterial-based speciation techniques.
- Recent developments and applications of nanomaterials in element speciation assays.
- Important trends in speciation research in environmental science and biomedicine.
- Novel platforms combining nanomaterials and microfluidics for elemental speciation.

GRAPHICAL ABSTRACT

NANOMATERIALS-BASED TE SPECIATION



ARTICLE INFO

Article history:

Received 24 September 2014

Received in revised form 11 February 2015

Accepted 16 February 2015

Available online 18 February 2015

Keywords:

Nanomaterials

Microanalytical systems

Speciation

Trace elements

ABSTRACT

Trace element speciation in biomedical and environmental science has gained increasing attention over the past decade as researchers have begun to realize its importance in toxicological studies. Several nanomaterials, including titanium dioxide nanoparticles (nano-TiO₂), carbon nanotubes (CNTs), and magnetic nanoparticles (MNPs), have been used as sorbents to separate and preconcentrate trace element species prior to detection through mass spectrometry or optical spectroscopy. Recently, these nanomaterial-based speciation techniques have been integrated with microfluidics to minimize sample and reagent consumption and simplify analyses. This review provides a critical look into the present state and recent applications of nanomaterial-based microanalytical systems in the speciation of trace elements. The adsorption and preconcentration efficiencies, sample volume requirements, and detection limits of these nanomaterial-based speciation techniques are detailed, and their applications in environmental and biological analyses are discussed. Current perspectives and future trends into the increasing use of nanomaterial-based microfluidic techniques for trace element speciation are highlighted.

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1. Introduction

The analysis of trace elements in biological and environmental samples is important because they play crucial roles in human life. Several analytical instruments, including atomic absorption spectroscopy (AAS), atomic fluorescence spectroscopy (AFS), inductively coupled plasma optical emission spectroscopy (ICP-OES), and inductively coupled plasma mass spectrometry (ICP-MS), can be used to analyze the total amounts of trace elements in biological, environmental, and food samples. Sample pretreatment (e.g., acid digestion [1]) is usually required to minimize matrix interference, but it can be laborious, costly, and environmentally unfriendly. Accordingly, for many analytical methods, focus has been placed on applying simpler sample pretreatment steps, such as dilution [2], extraction, filtration, solubilization [3], liquid–liquid extraction (LLE) [4–6], co-precipitation [7–9], solid phase extraction (SPE) [10–12], membrane filtration [13–15], and cloud-point extraction (CPE) [16–18]. These pretreatment methods can be used to separate and preconcentrate trace elements while eliminating matrix interference, resulting in high enrichments and recoveries.

Although these sample pretreatment methods have made trace element assays more convenient, they often require large sample or reagent volumes (several tens to hundreds of milliliters) to obtain high enrichment factors (EFs) or preconcentration factors (PFs). In cases where it is difficult or impossible to obtain such large sample volumes, these techniques often provide low EFs, resulting in high detection limits. To overcome these obstacles and improve analytical efficiencies, various materials have been tested to increase the sorption, extraction, and preconcentration of trace elements. Among these, nanomaterials are attracting increasing attention because of their specific binding affinities toward analyte elements; nanomaterials functionalized with various groups (e.g., chelating resins, peptides, proteins, and even other elements) can exhibit highly specific binding affinities. To date, nanomaterials have been used largely and effectively as SPE sorbents for the separation and preconcentration of analyte elements in total content analyses.

Although total content analysis of trace elements is important, their speciation is just as necessary. Trace element species exist in different oxidation states when in the form of free ions and nanoparticles, or as inorganic and organic complexes. Many

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