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Determination of gold nanoparticles in environmental water samples by second-order optical scattering using dithiotreitol-functionalized CdS quantum dots after cloud point extraction

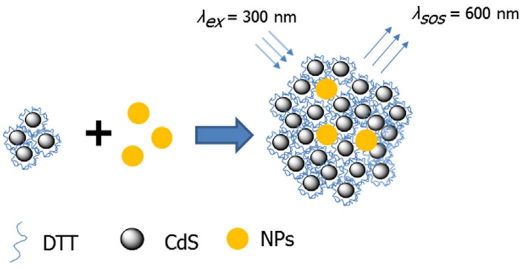
Spyridoula P. Mandyla, George Z. Tsogas, Athanasios G. Vlessidis, Dimosthenis L. Giokas*

Department of Chemistry, University of Ioannina, 45110 Ioannina, Greece

HIGHLIGHTS

- A new method has been developed to determine gold nanoparticles in water samples.
- Extraction was achieved by cloud point extraction.
- A nano-hybrid assembly between AuNPs and dithiol-coated quantum dots was formulated.
- Detection was accomplished at picomolar levels by second-order light scattering.
- The method was selective against ionic gold and other nanoparticle species.

GRAPHICAL ABSTRACT



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ABSTRACT

This work presents a new method for the sensitive and selective determination of gold nanoparticles in water samples. The method combines a sample preparation and enrichment step based on cloud point extraction with a new detection motif that relies on the optical incoherent light scattering of a nano-hybrid assembly that is formed by hydrogen bond interactions between gold nanoparticles and dithiotreitol-functionalized CdS quantum dots. The experimental parameters affecting the extraction and detection of gold nanoparticles were optimized and evaluated to the analysis of gold nanoparticles of variable size and surface coating. The selectivity of the method against gold ions and other nanoparticle species was also evaluated under different conditions reminiscent to those usually found in natural water samples. The developed method was applied to the analysis of gold nanoparticles in natural waters and wastewater with satisfactory results in terms of sensitivity (detection limit at the low pmol L^{-1} levels), recoveries (>80%) and reproducibility (<9%). Compared to other methods employing molecular spectrometry for metal nanoparticle analysis, the developed method offers improved sensitivity and it is easy-to-operate thus providing an additional tool for the monitoring and the assessment of nanoparticles toxicity and hazards in the environment.

1. Introduction

In the past few years, engineered nanoparticles have been the driving force for the development of new technologies in various applications owing to their unique physicochemical and optoelectronic properties. However, as their production and use rises, the

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* Corresponding author.
E-mail address: dgiokas@cc.uoi.gr (D.L. Giokas).

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environmental levels of nanoparticles are expected to increase mainly due to their occurrence in waste streams and direct emission pathways [1]. As a result, several regulation authorities have classified nanoparticles as emerging contaminants due to their potential environmental and health impacts. Hence, there is an increasing demand for appropriate analytical methods that would enable the efficient determination of nanoparticles in environmental samples.

The development of analytical methods for the determination of nanoparticles in environmental samples typically involves the combination of a sample preparation procedure with an appropriate detection technique. A variety of nanoparticle separation and enrichment methods have been described that involve both instrumental (e.g. field-flow fractionation, chromatography) [2–6] as well as off-line extraction procedures (e.g. liquid–liquid extraction, solid phase extraction, cloud point extraction, liquid or solid phase mixtroextraction etc) [7–12]. Of these methods, cloud point extraction (CPE) has received most attention owing to its simplicity and ease of operation, high enrichment factors, increased extraction efficiency and compatibility with most instrumental detectors [10,13–16]. With regards to identification and quantification of nanoparticles, atomic detectors such as ETAAS and ICP-MS are commonly utilized [3,9–16]. These detectors offer high selectivity and sensitivity and enable the determination of nanoparticles as their precursor metal ions at ultra-trace levels but they are costly and sometimes require sophisticated equipment and complex as well as time-consuming experimental procedures. On the other hand, owing to sensitivity and selectivity barriers the deployment of molecular spectrometry for the trace analysis of nanoparticles is still scarce. Only recently, we and others have demonstrated the potential of molecular spectroscopy for the determination of nanoparticles in environmental samples using molecular emission detectors such as fluorescence and chemiluminescence [17–19]. However, the majority of methods that rely on molecular emission enable the determination of nanoparticle species at relatively high concentration levels (i.e nmol L^{-1}) as compared to the predicted environmental concentrations of nanoparticles in natural waters (i.e femtomol L^{-1} to picomol L^{-1}) [20]. Therefore, analytical methods that can accomplish the determination of nanoparticles at ultra-trace levels are still in demand.

Scattering of light radiation by a solution containing dispersed particulate matter is a well-known phenomenon in optical detection methods and is used in nephelomteric detectors to measure the scattered radiation at a 90° angle to that of the radiation source. A similar phenomenon occurs in spectrofluorimetric detectors due to diffraction of light from the monochromator grating which passes through the emission monochromator and is detected as a peak at twice the excitation wavelength [21]. This diffraction is called second-order diffraction of scattered excitation light (or second-order scattering–SOS) and it is a non-linear optical scattering phenomenon that has been typically dealt as an unwanted source of light and it was suppressed or eliminated using optical long-pass filters.

The intensity of second-order scattered light, in analogy to nephelometry, is proportional to the concentration of the scattering particles provided that they are sufficiently separated from each other [22,23]. On the basis of this principle several studies have used SOS as an analytical detection strategy after reaction of the target analytes with specific reagents in order to form a suspension of ion-association aggregates which are large enough to scatter the incident light. This approach has been applied to the determination of micro-amounts of therapeutic drugs [24,25], biomacromolecules such as nucleic acids and proteins [26,27], anti-coagulation agents [28], food additives [29] and as an alternative detection strategy for non-fluorescence compounds (e.g. oligomers, saccharides, etc) in liquid chromatography [30]. Recently, scattering of light at double the incident wavelength has been observed in concentrated solutions of organic and inorganic nanoparticles and has been utilized for the investigation of nanoparticle properties in standard solutions [31,32] or as a template for the detection of analytes that can interact with nanoparticles and induce their aggregation [33]. However, the use of SOS for the determination of nanoparticles at ultra-trace levels has not been investigated.

The purpose of this work is to describe the development of a new and expedient analytical methodology for quantification of nanoparticles in aqueous solutions that provides enhanced sensitivity and selectivity compared to previous methods based on molecular spectrometry detectors. Gold nanoparticles which are probably the most widely utilized nanoparticles today [3] were effectively extracted and preconcentrated simultaneously from water samples by means of cloud point extraction. Detection was accomplished using a standard nephelometric experimental setup based on the optical incoherent light scattering, which depends linearly on the concentration of the scatter centers [23]. These centers were generated by the formation of a nano-hybrid assembly between dithiol functionalized CdS quantum dots and gold nanoparticles, and scatter the excitation light at double wavelength. The method was successfully applied to the determination of gold nanoparticles in environmental samples with high sensitivity and good selectivity against other nanoparticle species and metal ions.

2. Experimental

2.1. Materials

All reagents used were of analytical grade. Hydrogen tetrachloroaurate trihydrate (≥99.9% trace metals basis), sodium borohydride, tri-sodium citrate, polyvinyl pyrrolidone (PVP_{10}, average MW 10,000), polyvinyl alcohol (PVA, average MW 22,000), cetyltrimethylammonium bromide (CTAB), DL-dithiotreitol solution (1.0 M), sodium sulfide nonahydrate, sodium nitrate and humic acid dry powder were obtained from Sigma-Aldrich (Steinheim, Germany). Triton X-114 (TX-114), EDTA disodium salt, cadmium nitrate tetrahydrate and sodium thiosulphate were procured from Merck (Darmstadt, Germany). ZnO nanoparticles dispersion (35–100 nm) was purchased from Sigma-Aldrich. A dispersion of 1 mg L^{-1} was prepared in water under vigorous mixing. Immediately before sampling the mixture was re-suspended under ultrasound irradiation for 5 min.

2.2. Instrumentation

The UV/Vis spectra of nanoparticle solutions were recorded in matched quartz cells of 1 cm path length in a Jenway 6405 UV/Vis spectrophotometer. Second-order scattering was measured in a Varian Cary Eclipse spectrofluorimeter with 1 cm-thick quartz cuvettes. No low-pass or high-pass optical filters were used to suppress second order satellite lines from the diffraction gratings of the spectrofluorimeter. The size of the nano-hybrid assemblies was measured with a laser diffraction particle size analyzer (Shimadzu SALD-2300) using a 12 mL batch cell under stirring.

2.3. Methods

2.3.1. Synthesis of gold nanoparticles

The experimental procedures for the synthesis of golf nanoparticles were adopted from the literature. Detailed information on the synthetic procedures and characterization can be found in the Supplementary Information.

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