



Ultra-trace determination of gold nanoparticles in environmental water by surfactant assisted dispersive liquid liquid microextraction coupled with electrothermal vaporization-inductively coupled plasma-mass spectrometry



Ying Liu, Man He, Beibei Chen, Bin Hu *

Key Laboratory of Analytical Chemistry for Biology and Medicine (Ministry of Education), Department of Chemistry, Wuhan University, Wuhan 430072, PR China

ARTICLE INFO

Article history:

Received 7 September 2015
Received in revised form 2 March 2016
Accepted 27 April 2016
Available online 7 May 2016

Keywords:

Gold nanoparticles
Surfactant assisted dispersive liquid liquid microextraction
Electrothermal vaporization inductively coupled plasma mass spectrometry
Environmental water samples

ABSTRACT

A new method by coupling surfactant assisted dispersive liquid liquid microextraction (SA-DLLME) with electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) was proposed for the analysis of gold nanoparticles (AuNPs) in environmental water samples. Effective separation of AuNPs from ionic gold species was achieved by using sodium thiosulphate as a complexing agent. Various experimental parameters affecting SA-DLLME of AuNPs, such as the organic solvent, organic solvent volume, pH of the sample, the kind of surfactant, surfactant concentration, vortex time, speed of centrifugation, centrifugation time, and different coating as well as sizes of AuNPs were investigated carefully. Furthermore, the interference of coexisting ions, dissolved organic matter (DOM) and other metal nanoparticles (NPs) were studied. Under the optimal conditions, a detection limit of 2.2 ng L^{-1} and an enrichment factor of 152-fold was achieved for AuNPs, and the original morphology of the AuNPs could be maintained during the extraction process. The developed method was successfully applied for the analysis of AuNPs in environmental water samples, including tap water, the East Lake water, and the Yangtze River water, with recoveries in the range of 89.6–102%. Compared with the established methods for metal NPs analysis, the proposed method has the merits of simple and fast operation, low detection limit, high selectivity, good tolerance to the sample matrix and no digestion or dilution required. It provides an efficient quantification methodology for monitoring AuNPs' pollution in the environmental water and evaluating its toxicity.

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1. Introduction

Nanoparticles (NPs) have provided a unique basis for innovation in a wide variety of fields such as chemistry, medicine, electronics, biology, and material sciences. Among them, gold nanoparticles (AuNPs) have been applied in biomedical imaging [1], cancer therapy and diagnostics [2], biological and chemical sensing [3]. Due to their large quantity of production and widespread applications, AuNPs will inevitably be released into the environment. It is predicted that AuNPs are expected to reach a concentration of 140 ng L^{-1} in environmental waters within the next 10 years [4]. Therefore, the adverse effects of AuNPs are becoming one of the focuses of current research. It has been reported that many properties including shape, size, and coatings of the AuNPs have impact on the adverse effects and even toxicity in the organisms [5–7], and the cytotoxic effects of AuNPs on model human skin [8], lung [9] and stem cells [10] have been demonstrated. However, the information about the occurrence, fate, and toxicity of AuNPs is very

limited at present, partly due to the lack of quantitative methodology for AuNPs analysis in environmental and biological samples. Therefore, the development of simple, sensitive and accurate analytical methods for rapid determination of trace AuNPs in water samples is of great significance to the environmental pollution monitoring and the toxicity evaluation of metal NPs.

Up to now, various analytical methods have been developed for the determination of AuNPs, such as electrochemical methods [11], ultraviolet (UV) spectroscopy [12], Raman spectroscopy [12], energy dispersive X-ray fluorescence [13], atomic absorption spectrometry (AAS) [14] and inductively coupled plasma mass spectrometry (ICP-MS) [15, 16]. Among them, ICP-MS is considered to be one of the most powerful techniques for NPs analysis because of its high sensitivity, wide dynamic linear range and multi-element capability. Recently, single particle (SP) ICP-MS has been proposed for ultra-trace analysis of metal NPs [17,18] with particle size larger than 20 nm [19]. However, the direct determination of AuNPs in real-world environmental samples is a challenging task due to the expected very low concentration level of AuNPs in the samples and the very complex sample matrix. Hence, a step of separation and preconcentration of AuNPs is usually required prior to ICP-

* Corresponding author.

E-mail address: binhu@whu.edu.cn (B. Hu).

MS analysis. Traditional sample pretreatment methods such as centrifugation [20], filtration [21], and dialysis have been developed for separation and preconcentration of NPs from aqueous phase, they are time-consuming, operation troublesome, and easy to cause aggregation of NPs. Moreover, a size-selective approach like field-flow fractionation [22] has been employed for the analysis of AuNPs. However, this method suffers from incomplete recovery and analyte loss on instrument surfaces [23].

As a consequence, some new methods such as solid phase extraction (SPE) [24,25], magnetic solid phase extraction (MSPE) [26], capillary microextraction (CME) [16] and cloud point extraction (CPE) [27] have been developed for the separation and preconcentration of metal NPs. CPE was firstly introduced into the separation and preconcentration of silver nanoparticles (AgNPs) by Liu et al. [27]. By using ICP-MS for quantification, a LOD of 6 ng L^{-1} was achieved for Ag NPs with recovery ranging from 57 to 116% for spiked environmental samples. This strategy has the merits of strong anti-interference ability, high enrichment factor and keeping the size and shape of NPs. However, acid digestion and further dilution to 50–100 mL was used prior to ICP-MS determination. This makes the analytical method laborious and time-consuming. Later on, the CPE method was extended to the analysis of AuNPs [14], AgNPs [28], iron oxide nanoparticles [29], zinc oxide nanoparticles [30] and copper (II) oxide nanoparticles [31] in environmental waters. Schuster et al. [14,32] reported a CPE method for the extraction of AgNPs [32] and AuNPs [14] with electrothermal atomic absorption spectrometry (ETAAS) for quantification. Although acid digestion is not required, two hour incubation is needed. Moreover, due to the relatively high viscosity, the rich-surfactant phase should be dissolved with ethanol before introducing into ETAAS. Leopold et al. [25] developed a new SPE method followed by a ligand-assisted liquid extraction for separation and preconcentration of AuNPs from aqueous samples. However, the desorption time was above 3 h. In our previous work [26], we developed a MSPE-ICP-MS method for the simultaneous analysis of AuNPs and Au ions in environmental water. With self-prepared Al^{3+} immobilized $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{iminodiacetic acid}$ nanoparticles as the adsorbent, AuNPs and Au ions could be simultaneously retained on this adsorbent and their separation was achieved by sequential elution of Au ions and AuNPs with $\text{Na}_2\text{S}_2\text{O}_3$ and $\text{NH}_3 \cdot \text{H}_2\text{O}$, respectively. This method is sensitive, faster, easy-to-operate and no digestion required. Very recently, we proposed an online method by online coupling poly(AA-VP-Bis) monolithic CME with ICP-MS for the analysis of trace AuNPs in environmental water samples [16], and the sample throughput was 6 h^{-1} .

Dispersive liquid–liquid microextraction (DLLME), as an interesting and valid alternative in liquid phase microextraction, is a simple and fast microextraction technique based on a ternary component solvent system. The advantages of DLLME include simple operation, rapidity, low cost, low consumption of organic solvents and high enrichment factor. Since its introduction by Assadi and co-workers in 2006 [33], DLLME has been successfully applied to the analysis of organic pollutant [34], trace metals and their species [35,36] in environmental samples. In DLLME, an organic solvent which is soluble in the extraction solvent and miscible with water is required as a dispersant to assist the formation of fine oil droplets. However, the usage of conventional dispersant could decrease the partition coefficient of analytes into the extraction solvent [37], and increase the consumption of hazardous organic solvents. Consequently, surfactant was used as dispersant or emulsifier for enhancing the dispersion of extraction solvent in aqueous phase. In 2010, Yamini et al. [38] used surfactant-assisted dispersive liquid–liquid microextraction (SA-DLLME) for sample preparation in the analysis of chlorophenols in water samples. In this method, an environmental friendly ionic surfactant is used to disperse solvent in water samples instead of toxic organic solvent. Surfactants are organic compounds that contain both hydrophobic and hydrophilic groups, and soluble in both organic solvent and water. They can reduce the interfacial tension between the two phases by adsorbing at the liquid–liquid interface and

serve as an emulsifier to enhance the mass-transfer rate from aqueous samples to the extraction solvent. Hence, SA-DLLME has been successfully applied to the determination of organic compounds [39,40], trace metals and their species [41,42] in various samples. However, to the best of our knowledge, there is no report about the extraction of NPs by SA-DLLME so far.

The aim of this work is to explore the applicability of SA-DLLME in the separation and preconcentration of AuNPs from environmental water samples. By combining SA-DLLME with electrothermal vaporization (ETV), a microamount sample introduction technique, a method of SA-DLLME-ETV-ICP-MS was developed for the determination of AuNPs in environmental samples, without acid digestion and any further dilution. Experimental parameters affecting the extraction efficiency of SA-DLLME and ETV-ICP-MS determination were studied in detail. The proposed method was applied to the analysis of AuNPs in different environmental water samples for validation.

2. Experimental

2.1. Instrumentation

The determination of AuNPs was performed on an Agilent ICP-MS (7500a, Tokyo, Japan) equipped with a modified commercially available WF-4C graphite furnace (Beijing Second Optics, China) as electrothermal vaporizer. Details on the modification of the graphite furnace and its connection with ICP-MS have been described previously [43]. The polyethylene tubing transfer line (6 mm i.d.) had a total length of 70 cm. Optimization of the ICP-MS instrument was performed with a conventional pneumatic nebulization (PN) sampling mode prior to connection with the ETV device. Pyrolytic graphite coated graphite tubes were used throughout the work. The operating conditions for ETV-ICP-MS and the temperature program for the determination of AuNPs were summarized in Table 1. The transmission electron micrograph (TEM) images of the AuNPs were captured on a JEM-2010 electron microscope (Tokyo, Japan). Solution pH was adjusted with a Mettler Toledo 320-S pH meter (Mettler Toledo Instruments Co. Ltd., Shanghai, China).

2.2. Standard solutions and reagents

$\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ (Sigma-Aldrich, MO, USA) was used for the preparation of Au NPs and a free Au ions standard solution. Sodium citrate was purchased from Sigma-Aldrich. Polyvinylpyrrolidone (PVP, K-30), Cetyltrimethylammonium bromide (CTAB), Triton X-100 (TX-100), $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, and HCl (38%, w/w) were bought from Sinopharm

Table 1
Operating conditions of ETV-ICP-MS.

ICP-MS	
RF power	1200 W
Plasma gas	15.0 L min^{-1}
Auxiliary gas	0.9 L min^{-1}
Carrier gas	0.7 L min^{-1}
Sampling depth	7.0 mm
Sampler/skimmer diameter orifice	Nickel 1.0 mm/0.4 mm
Peak pattern	Peak-hop transient
Dwell time	50 ms
Integration mode	Peak area
Isotopes for detection	^{197}Au
Electrothermal vaporizer	
Injection volume	10 μL
Carrier gas	0.4 L min^{-1}
Drying	$110 \text{ }^\circ\text{C}$ ramp 5 s, hold 5 s
Pyrolysis	$300 \text{ }^\circ\text{C}$ ramp 10 s, hold 15 s
Vaporization	$2200 \text{ }^\circ\text{C}$, hold 4 s
Cooling	$100 \text{ }^\circ\text{C}$, hold 5 s
Cleaning	$2400 \text{ }^\circ\text{C}$, hold 3 s

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