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# Simultaneous determination of silver and gold nanoparticles by cloud point extraction and total reflection X-ray fluorescence analysis☆

Z. Bahadir[a,b,*], L. Torrent[b], M. Hidalgo[b], E. Marguí[b]

[a] Department of Chemistry, Faculty of Sciences and Arts, Giresun University, 28100 Giresun, Turkey
[b] Department of Chemistry, Faculty of Sciences, University of Girona, C/M. Aurèlia Campmany 69, 17003 Girona, Spain

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ABSTRACT

While the nanoscale dimensions give metallic nanoparticles unique physical and chemical properties, their potential release in the environment and subsequent effects on ecosystem health are becoming an increasing concern. In the present contribution, for the first time, a novel and simple analytical approach has been developed for the simultaneous quantification of silver and gold nanoparticles (AgNPs, AuNPs) in aqueous samples. The method combines a sample preparation and enrichment step based on cloud point extraction (CPE) with total reflection X-ray fluorescence spectrometry (TXRF) detection. Experimental conditions enabling the simultaneous extraction and detection of AgNPs and AuNPs were studied in detail. Under the best analytical conditions, limits of detection for AgNPs and AuNPs were 0.3 and 0.2 μg $L^{-1}$, respectively. Due to the lack of suitable certified references materials, accuracy of the CPE-TXRF method was tested by analysing several types of spiked water samples, including mineral, tap, river and sea water. Percentage recoveries achieved for the analysis of spiked samples were in all cases in the range of 82–100% for both types of studied NPs, suggesting that the existence of natural colloids, ionic $Ag^{+}$ and $Au^{3+}$ species, and other components in environmental waters have little influence on the quantitative determination of AgNPs and AuNPs. The only exception was the recovery obtained in the analysis of the spiked sea water sample that was around 40–50%. However, for salty aqueous samples, the developed analytical approach might still be feasible if the standard addition method is used for calibration purposes. In an attempt to provide additional information on AgNPs and AuNPs behaviour in the environment, the CPE-TXRF method was also applied to study the influence of organic matter content in waters as well as the influence of soil matrix on AgNPs and AuNPs stability.

## 1. Introduction

Because of their unique physical and chemical properties, the use of metallic nanoparticles (MNPs) has been considerably increased in various fields last years, being gold NPs (AuNPs) and silver NPs (AgNPs) the most commonly used [1]. AuNPs have been extensively used in medical applications, separation sciences, disease diagnostics and pharmaceuticals [2] while AgNPs have been mostly employed in medical devices and consumer products due to their excellent antibacterial properties [3]. Therefore, due to the increasing use of MNPs, a new concern has arisen about their presence in the environment. Although MNPs are not regulated yet, they are already included in lists of emerging pollutants [4] and their negative effect and potential toxic impact have been already confirmed in many studies [5,6].

To assess the behaviour of MNPs in the environment and their potential impact to human health is of prime importance to have suitable analytical methodologies to detect, characterize and quantify them. This is extremely challenging due to their small size, very low concentrations and the complexity of environmental matrices [7]. Another difficult issue is the discrimination of NPs from and ionic species of the same metal. Real samples may contain small quantities of metal ions that could be erroneously determined with NPs [8]. For this reason, the development of analytical methodologies to monitor MNPs in the environment is one of the current research topics in modern analytical chemistry. Several analytical approaches have been developed in the last few years for the characterization and determination of NPs [9,10]. An interesting analytical approach is the combination of a separation/preconcentration step followed by an atomic spectroscopic technique

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* Corresponding author at: Department of Chemistry, Faculty of Sciences and Arts, Giresun University, 28100 Giresun, Turkey.
*E-mail address:* zekeriyyabahadir@gmail.com (Z. Bahadir).

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**Table 1**
Summary of cloud point extraction based analytical procedures published last years for AgNPs and AuNPs quantification in aqueous samples.

| NPs | Sample treatment after CPE | Detection technique | LOD ($\mu g\,L^{-1}$) | Matrix | Ref. |
|---|---|---|---|---|---|
| Ag | Acidic digestion | ICP-MS | 0.006 | Water samples | [15] |
| Ag | Acidic digestion | ICP-MS | 0.12[a] | Antibacterial products | [16] |
| Ag | Acidic digestion | ICP-MS | 0.005 | Water samples | [17] |
| Ag | None | ETAAS | 0.002 | Water samples and lixiviates | [18] |
| Ag | Dissolution with ethanol | ETAAS | 0.0007 | Water samples | [19] |
| Ag | Evaporation and redissolution | TXRF | 0.7 | Antibacterial products and soil extracts | [20] |
| Au | Acidic digestion | ICP-MS | $ng\,kg^{-1}$ level | Soil extracts | [7] |
| Au | Dissolution with ethanol | ETAAS | 0.005 | Water samples | [21] |
| Au | Treatment with functionalized CdS quantum dots | OILS[b] | $pmol\,L^{-1}$ level | Water samples | [22] |
| Ag + Au | Evaporation and redissolution | CL[c] | 0.0002 | Water samples | [8] |

[a] $\mu g\,kg^{-1}$.
[b] OILS: optical incoherent light scattering.
[c] CL: chemiluminiscence.

[11,12]. In this category is important to emphasize the recent use of cloud point extraction (CPE) as a promising environment-friendly approach for separation and preconcentration of metal nano-materials [13]. In CPE procedure, hydrophobic analytes are encapsulated in micelles after the addition of a non-ionic surfactant and concentrated to a small volume with the assistance of centrifugation. CPE lies in the green analytical chemistry rules due to the little solvent consumption, low toxicity and inexpensive waste-disposal costs [14]. The possibility to use CPE for separation/preconcentration of different types of NPs was outlined by Liu et al. in 2009 [15]. Since then, only few researchers have used optimized CPE procedures for reliable quantification of MNPs. In Table 1 a summary of the CPE based analytical procedures published so far for AgNPs and AuNPs quantification is displayed. As it is shown in Table 1, inductively coupled plasma mass spectrometry (ICP-MS) detection has been successfully applied in combination with CPE for the determination of AgNPs as well AuNPs in water samples and soil extracts at environmental relevant concentrations. However, when combining CPE with ICP-MS detection, after the extraction step, the viscous micelle-rich phase has to be digested to enable the sample injection into the analytical instrument [7,15–17]. This fact increases the overall analysis time and limit the application in real NPs monitoring studies. The microanalytical capability of electrothermal atomic absorption spectrometry (ETAAS) has promoted the use of this technique also in combination with CPE. Using this approach, a sample digestion is not needed and the preconcentrated sample is usually analysed without any sample treatment or dissolved with few millilitres of ethanol [18,19,21]. This fact reduces the total analysis time and improves AgNPs and AuNPs limits of detection. Other detection techniques less used in combination with CPE include total reflection X-ray fluorescence spectrometry (TXRF) [20] and optical incoherent light scattering (OILS) [22].It is interesting to remark that in both cases an exhaustive sample treatment is needed before the final detection. For instance, the formation of a nano-hybrid assembly resulting from the hydrogen bond interactions between AuNPs and dithiotreitol functionalized CdS quantum dots is required after the CPE and before the OILS detection.

As it can be seen in Table 1, analytical methods enabling the simultaneous determination of various nanoparticles are still scant. At present there is only one publication about the simultaneous isolation of AgNPs, AuNPs and $Fe_3O_4$NPs [8]. However, in this method, after the CPE procedure, several selective back-extraction procedures are performed to achieve precursor metallic ions before the sequential chemiluminiscence detection. Therefore, it is a quite consuming procedure requiring 5 h to complete the analysis. This fact may limit the use of this method for routine purposes.

In a previous contribution we evaluated the possibilities and drawbacks of CPE-TXRF for AgNPs determination in consumer product water extracts and we studied in detail the effect of the AgNPs coating and size by comparing the obtained results with single particle inductively coupled plasma mass spectrometry (SP-ICPMS) [20].

Taking into account that real aqueous samples usually contain mixtures of different NPs types and the lack of multi-NPs analysis methods, the aim of the present contribution was the development of a simple analytical method for the simultaneous quantification of AgNPs and AuNPs in aqueous samples. Considering the multielemental capability of TXRF, the CPE procedure was used in combination with this technique. Experimental conditions enabling the simultaneous extraction and detection of AgNPs and AuNPs were studied in detail and the developed CPE-TXRF method was applied to the analysis of different types of spiked water samples (mineral, tap, river and sea water). Finally, the analytical approach was also used to study the influence of organic matter content in waters as well as the influence of soil matrix on AgNPs and AuNPs stability.

## 2. Experimental

### 2.1. Reagents, materials and apparatus

Commercial solutions of AgNPs (60 nm) and AuNPs (70 nm) stabilized with sodium citrate were purchased from NanoComposix (San Diego, USA). Gold and silver stock solutions of 1000 $mg\,L^{-1}$ were obtained from Merck (Darmstadt, Germany). Hydrochloric acid, nitric acid, sodium hydroxide, non-ionic surfactant Triton® X-114 and sodium thiosulfate pentahydrate were acquired from Sigma-Aldrich (Madrid, Spain). Working standard solutions were diluted with ultrapure water from a Milli-Q Plus system (Millipore Corp., Bedford).

pH measurements were measured by a digital pH meter (Crison, micro pH 2002) equipped with a glass-calomel electrode. Homogenization of nanoparticle dispersions was performed with an ultrasonic bath J.P. Selecta (Barcelona, Spain). Batch adsorption experiments were carried out using a rotary mixer Dinko (Barcelona, Spain). A centrifuge (Hettich-Zentrifugen, Lauenau, Germany) was used to assist phase separation of soil extracts and CPE surfactant rich NPs phase.

### 2.2. Samples

#### 2.2.1. Spiked water samples

In order to test the capability of the developed CPE-TXRF system for the simultaneous determination of AgNPs and AuNPs several types of water samples were considered including mineral, tap, river and sea water. In Table S1 (Appendix) chemical composition of these samples is displayed. These samples were analysed before and after a spiking procedure at the level of 5 $\mu g\,L^{-1}$ of AgNPs and AuNPs. To check the influence of the presence of ionic silver and gold species ($Ag^+$, $Au^{3+}$) on the determination of AgNPs and AuNPs, another aliquot of the aforementioned samples was spiked at the level of 5 $\mu g\,L^{-1}$ of AgNPs, 5 $\mu g\,L^{-1}$ of AuNPs, 10 $\mu g\,L^{-1}$ of $Ag^+$ and 10 $\mu g\,L^{-1}$ of $Au^{3+}$.

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