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Gold colloid analysis by inductively coupled plasma-mass spectrometry in a single particle mode

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Abstract

Analysis in a single particle mode of gold colloids in water has been performed by inductively coupled plasma-mass spectrometry (ICP-MS). The signal induced by the flash of ions due to the ionization of a colloid in the plasma torch can be measured for the ions $^{197}Au^{+}$ by the mass spectrometer without interferences. The intensity of the MS signal is recorded in time scan. The recorded peak distributions were analysed as a function of the colloid size for five monodisperse colloids (80–250 nm). This study describes the experimental conditions to analyse gold colloids in a single particle mode. The size detection limit is around 25 nm corresponding to 0.15 fg colloids and one particle per ml may be detected during a 1 min time scan within standard procedure.

Keywords: Single particle analysis; Inductively coupled plasma-mass spectrometry; ICP-MS; Gold colloid; Colloid size

1. Introduction

Single colloid analysis from suspension is generally performed after separation on filters followed by scanning electron microscopy (SEM) investigation [1]. Single particle analysis has been carried out for more than a decade utilising also light-based techniques such as laser-induced breakdown detection (LIBD), e.g. [2] or single particle counting (SPC) [3]. Recently, imaging of single-metal nanoparticles in scattering media was found to be more performant by photothermal interference than by ordinary differential interference contrast and allowed detection of 5 nm colloids [4]. These techniques quantify the number of particles per unit volume of fluid and have been applied to the analysis of natural water [5,6].

The conventional inductively coupled plasma-atomic emission spectrometry (ICP-AES) was successfully adapted by Borchet and Dannecker [7] for individual particle analysis. By this method, the particle introduction in the torch induces a transient emission signal that can be recorded and specifically analysed. This technique was adopted for aerosol analyses. These experiments provided information about the precision of the technique and the influence of matrix elements on the emission intensity. The technique was used for the analysis of sanding and abrasive dusts.

Mass spectrometry (MS) is one of the primary analysis methods for determining the chemical composition of small samples and several of these techniques have been adapted to analyse single aerosol particles [8], or after separation on a specific sample carrier, laser microprobe mass analysis (LAMMA) can be applied for single particle analysis [9].

The use of inductively coupled plasma-mass spectrometry (ICP-MS) for single particle analysis was pre-discussed for colloid bearing solutions by the author at the IUPAC meeting in Davos, Switzerland and published in [1]. Independently, Momizu et al. [10,11] successfully tested this approach for airborne particles at the fg level, by injecting the air-contaminated samples in the plasma torch. Recently, the feasibility of single particle ICP-MS analysis from a colloid suspension in water was tested for TiO_2, $A1_2O_3$ and clay [12], ZrO_2 colloids [13] and ThO_2 colloids [14].

Research on noble-metal nanoparticle emphasises size effect. Gold colloids find their applications in biology [15], e.g. as

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cytochemical markers [16] and medical fields [17]. In the latter, recently they have been found to be specifically functionalized with a variety of biomolecules including antibodies and streptovidine [18]. Gold colloids are currently used as a carrier in blood [19]. Finally, gold colloidal particles are occasionally used as a tracer in geoscience [20] and are locally analysed in surface water for prospection, e.g. [21].

In this work, the testing of single particle analysis from a gold colloid suspension in water was studied by ICP-MS, because these colloids are monoisotopic, monoatomic and monodisperse. The transient signal induced by the ionization of a colloidal particle in the plasma torch produces a flash of $^{197}Au^+$ ions that can be detected and measured by the mass spectrometer. Basic properties of this signal allow determination of the gold particle size and the colloid concentration.

2. Theoretical background

For single colloid analysis, the ICP-MS unit may be adapted using a colloid suspension injection system in the blank water stream when needed or used with the usual set up when the suspension is sufficiently diluted. The diluted colloid suspension is continuously introduced in the nebulizer producing an aerosol of micro-drops (1 micro-drop carrying one colloid among 10^5–10^6 micro-drops colloid free) in the argon flow feeding the inductively coupled plasma torch coupled to a mass spectrometer. With this system, the colloids are ionized in the plasma torch with a maximum frequency of one per recorded slot time.

A colloid suspension of metal M (molecular weight M_M ($g\,mol^{-1}$)) and of concentration N_{col} (cm^{-3}) is injected at a flow rate of q_{col} ($cm^3\,s^{-1}$) when required in the stream of blank water with a flow rate of q_{sol} ($cm^3\,s^{-1}$), or the diluted suspension is sprayed with a nebulization yield η_{neb} and transported in an argon flow of q_{Ar} ($cm^3\,s^{-1}$) into the plasma torch. The temperature of the torch T (K) allows the gas to warm up from room temperature, e.g. 300 K to T, with T/300 usually of the order of 20 [22]. Each single particle undergoes ionization and the intensity of the ion flash is a function of the size of the initial particle d (cm) and the frequency of these flashes f (s^{-1}) is a direct function of the colloid concentration N_{col} (cm^{-3}). A fraction η_A of the isotope ions $^AM^+$ (here mostly 100% for many elements, e.g. [23], referring to all M^{j+} ions, with $1 \leq j$) is produced in the plasma. Other ions MX^{k+} are yielded by reaction with reagents or atmospheric elements in the torch. The ion single flash passes through the cone hole, the skimmer and is detected by the mass spectrometer detector with a counting yield of η_c. The signal observed for a given ion mass as a function of time is a peak whose intensity or area is a function of the mass of the analysed colloid or of the fraction of the element and/or isotope in the colloid considered.

The number of M atoms N_M for a particle of size d (cm) is given by $N_M = \pi\rho N_{Av}(6M_M)^{-1}d^3$, where ρ ($g\,cm^{-3}$) is the colloid density and N_{Av} the Avogadro constant (mol^{-1}). The colloid exploding in the torch generates ions. An $^AM^+$ ion fraction passes through the spectrometer and the signal s_A per slot time Δt (s) is detected for the mass A (isotope ion $^AM^+$ or its interferences, e.g. $^{2A}M^{*2+}$ or $[^{A-16}M^{\#16}O]^+$) during the investigation. The number of atoms of M in the analysed colloid or the colloid size d is deduced from the signal s_A recorded during the measurement slot time by the expression: $s_A = \pi\eta_A\eta_c\rho(6M_M)^{-1}N_{Av}d^3$ or:

$$s_A = \xi d^3 \tag{1}$$

with $\xi = \pi\eta_A\eta_c\rho(6M_M)^{-1}N_{Av}$.

The colloid concentration N_{col} in the original suspension may be apparently diluted by a factor of q_{col}/q_{sol}. The fraction η_{neb} reduces the colloid fraction in the argon flow. Dilution is only valid for the dissolved species, however, the colloid as single entity remains entire and is not actually diluted. However, one colloid or no colloid must be detected during the detection slot time fixed during signal record. The frequency of signal s_A is noted $f(s_A)$ (s^{-1}) and is given by: $f(s_A) = N_{col}q_{col}\eta_{neb}$ or:

$$f = \phi N_{col} \tag{2}$$

with $\phi = q_{col}\eta_{neb}$. Both functions $s_A(d)$ and $f(N_{col})$ allow the size distribution, i.e. $N_{col}(d)$ for a given element (or isotope) in the colloid phase to be evaluated on the basis of the signal distribution $f(s_A)$.

3. Experimental

The concentration of gold colloid-stock suspensions (BB International, Cardiff, UK) depends on their size as given in Table 1. They were stirred for 2 min, to resuspend the colloids prior to dilution with a factor of 100. The stock solution that was stocked in obscurity at 4 °C was diluted in a flow box class or clean laboratory to a particle number concentration of the order of $10^6\,cm^{-3}$.

The scanning electron microscopy investigations were performed with a Zeiss DSM 962 unit under 30 kV. SEM investigations on the gold colloids were carried out with suspension contacted onto TEMFIX film and coated with 15 nm Pt layer by Magnetron sputtering prior to microscopic investigation.

Single particle counting investigations by light scattering was carried out at 780 nm (30 mW solid state laser) for 90° and for 10 runs of 1 min duration. Single particle monitor (HSLIS-M50) and single particle spectrometer (HVLIS-C200), both units from Particle Measuring Systems Inc. (PMS), Boulder, CO, were used on-line sequentially as described earlier [5]. Calibration was performed with latex particles (Duke Scientific Cooperation, Palo Alto, CA) of size 102 ± 3 nm, 199 ± 6 nm, 499 ± 5 nm and 701 ± 6 nm. For the measurements with these units, q_{sol} and q_{col} were, respectively, 6.0 $cm^3\,s^{-1}$ and $5 \times 10^{-3}\,cm^3\,s^{-1}$.

Table 1
Concentration and size of the standard colloidal solutions with coefficient of variation CV

Colloid size (nm); CV ~ 8%	Colloid concentration (ml^{-1})
81.1	1.1×10^{10}
100.2	5.5×10^{9}
146.7	1.7×10^{8}
203.8	7.0×10^{8}
249.8	3.6×10^{8}