



# Sedimentation field flow fractionation and optical absorption spectroscopy for a quantitative size characterization of silver nanoparticles



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## ABSTRACT

Many advanced industrial and biomedical applications that use silver nanoparticles (AgNPs), require that particles are not only nano-sized, but also well dispersed, not aggregated and not agglomerated. This study presents two methods able to give rapidly sizes of monodispersed AgNPs suspensions in the dimensional range of 20–100 nm.

The first method, based on the application of Mie's theory, determines the particle sizes from the values of the surface plasmon resonance wavelength ( $SPR_{MAX}$ ), read from the optical absorption spectra, recorded between 190 nm and 800 nm. The computed sizes were compared with those determined by transmission electron microscopy (TEM) and dynamic light scattering (DLS) and resulted in agreement with the nominal values in a range between 13% (for 20 nm NPs) and 1% (for 100 nm NPs).

The second method is based on the masterly combination of the Sedimentation Field Flow Fractionation (SdFFF – now sold as Centrifugal FFF-CFFF) and the Optical Absorption Spectroscopy (OAS) techniques to accomplish sizes and quantitative particle size distributions for monodispersed, non-aggregated AgNPs suspensions. The SdFFF separation abilities, well exploited to size NPs, greatly benefits from the application of Mie's theory to the UV–vis signal elaboration, producing quantitative mass-based particle size distributions, from which trusted number-sized particle size distributions can be derived. The silver mass distributions were verified and supported by detecting off-line the Ag concentration with the graphite furnace atomic absorption spectrometry (GF-AAS).

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## 1. Introduction

Silver nanoparticles (AgNPs), for their broad spectrum of antibacterial and fungicidal activities, are active constituents of a number of consumer products, including soaps, pastes, cosmetics, plastics, food packaging, textiles, wound dressings, biomedical devices and many others. AgNPs have also unique optical, electrical, and thermal properties that make them suitable to be incorporated into products that range from photovoltaics to biological and chemical sensors, such as conductive inks, pastes and fillers, photonic devices such as, for example, solar cells where AgNPs are used as plasmonic light traps. The economic interests around AgNPs are consequently important, as they are their market horizons.

AgNPs with different morphologies, sizes, and shapes to target specific applications can be nowadays easily synthesized; nevertheless, one of the critical criteria that has to be satisfied remains the size distribution that should be often as narrow as possible. This requirement has determined an increasing attention towards all those analytical methods, which are potentially able to give this information.

The family of analytical techniques termed Field-Flow Fractionation (FFF) has entered in the laboratory practice as a set of methods suitable to separate and characterize nano and micro particles, colloids, macromolecules, natural and synthetic polymers [1,2]. They are elution techniques, in which the detection varies depending on the method and the sample type. Common detectors might be UV–vis optical absorption spectrophotometer (OAS), multi-angle laser light scattering (MALLS), dynamic light scattering (DLS), refractive index (RI), or destructive detectors such as the graphite furnace atomic absorption spectrometer (GF-AAS), the inductively

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**Table 1**

Sizes information about the AgNPs given by the suppliers and measured with different techniques and theoretical approaches. \*The TEM sizes were chosen as the most reliable.

	Size (nm)					
	AgNP20	AgNP30*	AgNP40	AgNP60	AgNP70	AgNP100
Nominal	20	30	40	60	70	100
TEM*	19.6 ± 1.6	32.3 ± 3.2	40.6 ± 3.0	57.4 ± 4.0	68.4 ± 4.2	99.4 ± 7.0
DLS [7]	25	45	54	67)	69	98
Mie Fit – Palik	10	46	48	64	74	102
Mie Fit – J&C	60	60	62	74	80	106
SPR <sub>MAX</sub> – Palik	33	40	44	61	69	99
*Relative Error% (SPR <sub>MAX</sub> Palik)	65	25	7	7	1	–
SPR <sub>MAX</sub> – J&C	49	54	58	71	79	107
*Relative Error% (SPR <sub>MAX</sub> J&C)	49	69	41	24	16	8

coupled plasma atomic emission spectrometer (ICP-AES) or the inductively coupled plasma mass spectrometer (ICP-MS).

The Sedimentation FFF (SdFFF), and the Flow-FFF (F4) techniques are both suitable to analyze gold [3,4] and silver NPs [5–8]. For these specific applications, the simplest instrumental configuration involves the use of an UV–vis detector and an aqueous solvent as eluent medium. The analysis result is represented graphically by a fractogram (elugram), where the detector response is reported as a function of the analysis time (retention time). From these data it is possible to derive the particle size distribution (PSD) of the sample. However, the conversion of the fractogram into the PSD hides an important assumption connected to the proportionality between the detector signal and the sample concentration or the sample mass.

The linearity between the absorbance and the sample concentration, almost obvious for absorbing molecular species, becomes indeed more complicated in the case of particulate species, where the light scattering component adds to the absorbing component [9]. The absorption component remains mass proportional, while the scattering component follows complicated relations, which depend on the particle size (diameter  $d$ ) compared with the incident electromagnetic wavelength  $\lambda$  [9]. The use of Mie's theory in the FFF literature is limited to the cases in which the particle turbidity (scattering) was evaluated under the conditions that the ratio between the scattering coefficient and the particle diameter was constant and the refractive index of the sample was known [10,11].

The UV–vis signal of plasmonic NPs, such as the AgNPs, is by far more complicated, because both absorption and scattering of light depends in a nontrivial way on particles' size, shape, aggregation, dielectric environment, surface coating and even mutual electromagnetic interaction in nearby particles [12–14]. These correlations complicate the expressions describing the dependence of the OAS signal on NPs' concentration.

This study demonstrates firstly that the correct application of Mie's theory allows to determine quite rapidly and with a reasonable degree of accuracy the size of AgNPs aqueous suspensions, from the OAS spectra. The reliability of the evaluation is assessed by comparing the NP sizes, here comprised in the range 20–100 nm, with those achieved with other analytical techniques, such as transmission electron microscopy (TEM) and DLS [7]. Secondly, that the coupling on-line of the UV–vis detector (OAS) with a SdFFF allows to get a quantitative particle size distribution. This is possible since the SdFFF provides an independent and accurate determination of spherical particles' diameter from the measurement of the retention time, while the on-line OAS provides a signal that through the Mie's theory is related to the relative silver abundance of each size. The quantitative mass-based particle size distributions, elaborated from the fractograms, are therefore converted in number-sized PSD. The exactness of the quantitative PSD profiles is verified by

the off-line silver amount determination provided by the graphite furnace atomic absorption spectrometer (GF-AAS).

## 2. Theory

### 2.1. OAS spectrum modeling

Optical properties of AgNPs were calculated with Mie's theory, which is based on the solution of the Maxwell's equations in spherical coordinates using the multipoles expansion of the electric and magnetic fields and accounting for the discontinuity of the dielectric constant between the sphere and the surrounding medium [9]. Detailed information about the procedures are reported in the paragraph SM-2 of the Supplementary material (SM).

### 2.2. SdFFF-OAS coupling

The theory of SdFFF, is widely documented in literature [15–17]. However, for the sake of discussion, the paragraph SM-4 in the Supplementary material reports the fundamental relationships which govern the retention, the proportionality of the retention time with the particle sizes, and how, for a flow-through analysis, the optical absorbance and the extinction cross section  $\sigma_{ext}$  are used to get quantitative particle size distributions (mass or number frequency function  $F_{m,i}, F_{n,i}$ ).

## 3. Materials and methods

### 3.1. Reagents

Nearly monodisperse sodium citrate stabilized silver AgNPs dispersions of 20, 30, 40, 60, 70 and 100 nm at a nominal concentration of 20 mgL<sup>-1</sup> were kindly donated by the Joint Research Centre, Institute for Health and Consumer Protection, Ispra (Italy). To avoid silver particle degradation or precipitation, dispersions were stored at 4 °C and protected from prolonged exposure to light.

Information regarding the sizes and the actual total silver concentrations, determined with complementary techniques by the JRC are reported in Tables 1 and 2 respectively.

NaOH and sodium citrate (Carlo Erba Reagents – Italy) were used to prepare the mobile phase (eluent) for the SdFFF instrument.

All solutions were prepared using ultrapure deionised water (18 M $\Omega$  cm<sup>-1</sup>) obtained from a MilliQ system (Merck Millipore Milan, Italy).

### 3.2. SdFFF

A Colloid/Particle Fractionator SdFFF system (Model S101 Postnova Analytics, Landsberg, Germany), described in detail elsewhere [3,18], was employed to fractionate the AgNPs according to their buoyant mass. AgNP suspensions were injected through a 50  $\mu$ L

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