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A comparison study of chemiluminescence systems for the flow injection determination of silver nanoparticles

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ABSTRACT

The comprehensive study of various chemiluminescence systems (luminol, lucigenin, $KMnO_4$, Mn(IV), Ce(IV) and $K_3Fe(CN)_6$) in terms of their applicability to the detection of silver nanoparticles (AgNPs) has been carried out for the first time. Among the fourteen systems tested, Mn(IV)-formaldehyde-hexametaphosphate was selected as the optimal for the trace determination of AgNPs. The flow injection chemiluminescence method (FI-CL) based on enhancing effect of AgNPs on Mn(IV) chemiluminescence was developed. It was found that sensitivity of measurements depends on the size of AgNPs as well as the type of nanoparticles coating. Under the optimized conditions, the detection limits for AgNPs size fractions of 10 nm, 40 nm and 100 nm stabilized by sodium citrate were in the range 0.3–2.9 $\mu g\,L^{-1}$, AgNPs size fractions of 40 nm, 60 nm and 100 nm stabilized by polyethylene glycol (PEG) were in the range 2.7–13.3 $\mu g\,L^{-1}$, AgNPs size fractions of 20 nm and 75 nm stabilized by polyvinylpyrrolidone (PVP) were 20.2 $\mu g\,L^{-1}$ and 24.9 $\mu g\,L^{-1}$, respectively. Repeatability of the results expressed as a relative standard deviation (n = 10) was ≤3.3%. The developed method is simple and offers high sample throughput (150 samples per hour). The accuracy of the method was confirmed by analysis of the reference material RM 8017. The method was successfully applied to the direct determination of trace amounts of AgNPs in spiked natural mineral and tap water samples. The recoveries of AgNPs were in the range of 96.8–102%.

1. Introduction

Nano-size silver particles (AgNPs) have a broad spectrum of antimicrobial activity and therefore they are incorporated into various materials, including textiles (e.g. anti-odour sportswear, socks and gloves), food contact materials and other consumer products, such as disinfecting sprays, kitchen cutting boards, toothbrushes, toilet seats, water filters, blankets, pillows, mattresses, wet wipes, paints, etc. Food supplements and cosmetics labelled to contain nanosilver are also commercially available. According to the Nanotechnology Consumer Products Inventory database, silver is the most frequently used nanomaterial (442 products in 2018) [1]. The growing commercial application of silver nanoparticles will certainly increase the exposure to this nanomaterial among humans and in the environment. Therefore, reliable analytical methods are required for the determination of silver nanoparticles. The only method that allows direct determination of metallic nanoparticles at very low concentrations (at ng L^{-1} level) is single particle inductively coupled plasma mass spectrometry (sp-ICP MS) [2]. The capability of this technique to characterize metallic NPs in a variety of environmental samples and biological media has been demonstrated. However, the size detection limit of silver nanoparticles obtained by this technique is ~20 nm, which makes it impossible to determine smaller AgNPs. Moreover, the improvements in ICP MS instrument, such as very short detector dwell times (on the order of microseconds) and appropriate software are necessary to perform analysis. In the case of electrothermal atomic absorption spectrometry (ETAAS), the quantitative analysis of AgNPs at very low concentrations in various samples is possible after their extraction by cloud point extraction (CPE) technique [3]. However, this method could not directly provide the information on the size of nanoparticles. The simultaneous determination of the concentration and size of AgNPs is possible using hyphenated separation and detection techniques, such as flow field fractionation [4], capillary electrophoresis [5] and high performance liquid chromatography [6] coupled to ICP MS.

The chemiluminescence (CL) is a powerful analytical technique especially for the trace determination of metals. The most important features of CL methods are simple and inexpensive instrumentation and low limits of detection. The combination of chemiluminescence

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detection with flow injection analysis (FI-CL) reduces the time of analysis and ensures high precision and high sensitivity of measurements. Therefore, FI-CL methods have become an attractive alternative to other analytical methods.

Various nanomaterials (e.g. nanoparticles of silver, gold, platinum and iron(III) oxide, CdS quantum dots) have proved to be effective enhancers in the chemiluminescence reactions leading to improved sensitivity of CL methods [7,8]. The chemiluminescence reactions amplified by silver nanoparticles, their mechanisms and analytical applications have been recently reviewed [9]. Ability of AgNPs to increase the CL intensity is connected to their plasmonic, catalytic, reducing and energy accepting properties. The most studied systems are AgNPs-catalyzed luminol CL reactions. The enhancing effect of AgNPs on lucigenin, peroxyoxalate, $KMnO_4$, $K_3Fe(CN)_6$ and Ce(IV) chemiluminescence has also been demonstrated. These AgNPs-enhanced CL systems have been applied for developing sensitive analytical methods for the determination of drugs, amino acids, polyphenols and many others organic compounds [9]. The literature review showed that in some systems the CL intensity depends on the size and concentration of the AgNPs [10–13]. Chen et al. [10] studied the catalytic activity of AgNPs of different sizes (6.8–37.4 nm) on luminol-H_2O_2 CL reaction. They found that AgNPs with the smallest size (6.8 nm) displayed the best catalytic activity. Liu and Li [11] also investigated AgNPs of different diameters (5–40 nm) and found that the CL intensity of luminol-$AgNO_3$ system decreased with increasing nanoparticle size. The influence of AgNPs concentration on the luminol-based CL was also studied. The CL signal was linearly increasing with the concentration of AgNPs in the range from 2.2 to 5.4 μg mL^{-1} (in luminol-$KMnO_4$ CL system) [12] and from 8 to 26 μg mL^{-1} (in luminol-isoniazid CL system) [13]. The linear relationship between the CL intensity and the concentration of AgNPs implies that silver nanoparticles might be determined by the chemiluminescence methods.

To the best of our knowledge, there is only one paper on CL method for the determination of silver nanoparticles in the literature [14]. However, AgNPs were not involved in the chemiluminescence reaction, but they were first transformed into Ag(I) ions and these ions were detected by chemiluminogenic reaction of luminol. The procedure is quite complicated and time-consuming. The H_2O_2 solution was used to completely dissolve AgNPs. The solution containing the released Ag(I) ions was mixed with $K_2S_2O_8$, $MnSO_4$, and H_3PO_4 and heated at 90 °C to promote the catalytic action of Ag^+ towards the formation of $KMnO_4$. After cooling and neutralization with phosphate buffer solution, the sample was injected into the FI-CL system.

The objective of this study was to develop a direct method for chemiluminescent determination of silver nanoparticles. In order to select the most suitable chemiluminophore various CL systems, based on luminol, lucigenin, $KMnO_4$, Mn(IV), Ce(IV) and $K_3Fe(CN)_6$ reagents, were compared regarding their sensitivity to determine silver nanoparticles. The application of manganese(IV) reagent for the CL detection has been reviewed by Adcock et al. [15]. Manganese(IV) reacts with many compounds to produce an excited manganese(II) species that emit red light. The Mn(IV)-based CL system was applied in our former works for the determination of polyphenols in plant extracts and food products [16–18]. This CL system, in comparison to luminol-based systems, is characterized by better stability of the baseline and precision of the measurements. The literature survey shows that the effect of AgNPs on Mn(IV)-based chemiluminescence has not been studied yet.

This is the first work on the comparison of different CL systems for their applicability in AgNPs detection. Mn(IV)-formaldehyde-hexametaphosphate chemiluminescence system was selected as the optimal and FI-CL method for the determination of the AgNPs was developed. The trueness of the method was proved by analysis of spiked water samples and reference material of silver nanoparticles. The method was applied for the determination of trace amounts of AgNPs in drinking water.

2. Materials and methods

2.1. Reagents and solutions

All chemicals were of analytical grade and solutions were prepared in ultrapure water (18.2 MΩ·cm) obtained from Millipore Direct-Q 3 UV water purification system (France). Formaldehyde, sodium hydroxide, potassium hydroxide, sulphuric acid, sodium sulphite, potassium hexacyanoferrate(III), potassium iodide, sodium chloride, potassium sulphate, magnesium sulphate heptahydrate, calcium chloride hexahydrate, nickel chloride hexahydrate, sodium fluoride and sodium hydrogen carbonate were supplied by POCH (Poland). Ammonium cerium(IV) nitrate, sodium dodecyl sulphate (SDS), Tween 20, Triton X-100, rhodamine 6G, sodium citrate, fluorescein, isoniazid, terbium(III) chloride hexahydrate, cobalt(II) chloride, hydrogen peroxide, luminol, lucigenin and humic acid were obtained from Sigma-Aldrich. Sodium periodate was supplied by Carl Roth (Germany) and potassium periodate was from Roanal (Hungary).

Mn(IV) solution at the concentration of $1.7 \cdot 10^{-3}$ mol L^{-1} was prepared in 3 mol L^{-1} phosphoric acid (Chempur, Poland) according to the procedure described in our previous paper [16]. Briefly, manganese (IV) solution was obtained by dissolving freshly precipitated manganese dioxide (formed during the reaction of sodium formate (Sigma-Aldrich, USA) with potassium permanganate (POCH, Poland)) in 3 mol L^{-1} phosphoric acid. The mixture was ultrasonicated for 24 h and stored in the dark at an ambient temperature for the next four days. The CL reagent was prepared daily by dissolving an appropriate amount of sodium hexametaphosphate (Chempur, Poland) in acidic solution of $1.7 \cdot 10^{-3}$ mol L^{-1} manganese(IV).

Luminol stock solution ($2.5 \cdot 10^{-2}$ mol L^{-1}) was prepared by dissolving an appropriate amount of the compound in 0.1 mol L^{-1} NaOH solution and stored in a refrigerator for 24 h prior to use. Working solutions of luminol were prepared before use by dilution of the stock solution with NaOH solution. In the case of luminol-$K_3Fe(CN)_6$-fluorescein system, working solutions of luminol were prepared by dilution with borate buffer (pH 8.8).

Citrate stabilized AgNPs (solvent: $2 \cdot 10^{-3}$ mol L^{-1} sodium citrate) with nominal diameters of: 10 nm (9.5 ± 1.9 nm, mass concentration of Ag 0.021 mg mL^{-1}), 40 nm (40.7 ± 4.4 nm, 0.021 mg mL^{-1} Ag), 100 nm (104.3 ± 12.6 nm, 0.022 mg mL^{-1} Ag); PVP stabilized AgNPs (solvent: Milli-Q water) with nominal diameters of: 20 nm (19.3 ± 3.1 nm, 0.022 mg mL^{-1} Ag), 75 nm (77.5 ± 7.0 nm, 5.00 mg mL^{-1} Ag); PEG stabilized AgNPs (solvent: Milli-Q water) with nominal diameters of: 40 nm (39.0 ± 5.2 nm, 0.020 mg mL^{-1} Ag), 60 nm (59.6 ± 5.8 nm, 0.021 mg mL^{-1} Ag), 100 nm (103.0 ± 11.0 nm, 0.023 mg mL^{-1} Ag) were obtained from NanoComposix (USA). Citrate stabilized AgNPs with nominal diameters of 20 nm (20 ± 4 nm, 0.02 mg mL^{-1} Ag) and 60 nm (60 ± 8 nm, 0.02 mg mL^{-1} Ag) were obtained from Sigma-Aldrich (USA). The working solutions of silver nanoparticles were freshly prepared before measurements: the stock solutions were vigorously shaken (typically ~1 min) and diluted with $2 \cdot 10^{-3}$ mol L^{-1} sodium citrate solution (in the case of citrate stabilized nanoparticles) or Milli-Q water (in the case of PVP and PEG stabilized nanoparticles). Ag(I) standard (1000 mg L^{-1}, TraceCert) was supplied by Fluka (Switzerland).

Reference Material (RM) 8017 containing PVP-coated silver nanoparticles of nominal diameter 75 nm (74.6 ± 3.8 nm) was obtained from National Institute of Standards & Technology (NIST) (United States). The lyophilised PVP-coated silver nanoparticle cake (which contained nominally 2.162 ± 0.020 mg Ag) was reconstituted with 2 mL of ultra-pure water according to the manufacturer's instructions and stored tightly capped at +4 °C

2.2. Apparatus and procedure

The FI-CL systems used in this work are shown in Fig. 1. The solutions of sample, carrier and reagents were propelled by a peristaltic