Recent Extraction Techniques Used for Separation of Silver Nanoparticles from EnvironmentalMatrices: A Brief Review

Ingrid Hagarová

Comenius University in Bratislava, Faculty of Natural Sciences
Institute of Laboratory Research on Geomaterials, Slovak Republic

--**ABSTRACT**---
Due to the increasing production and use of engineered nanoparticles, it is expected that their concentration in various environmental compartments will grow up. This fact is related to the increasing demand of their reliable quantification in environmental matrices. However, the reliable quantification of nanoparticles in complex matrices is not an easy task. It is mainly due to extremely low concentrations of nanoparticles and complicated coexisting matrix. For this purpose, the adaptation of existing techniques and methods, or the development of new ones is necessary. Among engineered nanoparticles, silver nanoparticles (AgNPs) belong to the group of the most frequently used nanomaterials. This review demonstrates that a combination of well-established extraction procedures (namely liquid-liquid extraction, cloud point extraction, solid phase extraction, and magnetic solid phase extraction) and commonly available spectrometric methods can be considered as promising alternative for separation/preconcentration and quantification of AgNPs in various types of environmental waters and some antibacterial products.
KEYWORDS: Silver nanoparticles, Extraction techniques, Spectrometric methods, Natural waters

I. INTRODUCTION

The production of engineered nanoparticles (ENPs) has exponentially increased in the past two decades. It is due to their extensive use in medicine, biomedical products, pharmaceuticals, electronics, engineering materials, agriculture, personal care products and many other sectors [1,2]. As a consequence of their extensive use, their release into the various environmental compartments is increasing at a rapid pace. In spite ofindisputable advantages of ENPs, their potential health hazards cannot be overlooked precisely due to their uncontrollable use, increasing concentrations in the environment, and potential toxic effects. Thus, ENPs are considered as a new class of pollutant due to their unique properties and extraordinary behaviors, which leads to the unknown environmental risks [3-6]. Finding answers to questions about behavior of ENPs in the environment, analytical chemists focus their attention to the development of different procedures for their reliable detection, identification, characterization and quantification, not only in homogenous and simple matrices, but also in complex environmental matrices[7,8].

Among ENPs, metal-based nanoparticles have irreplaceable place. Pure metals (e.g., Au, Ag, Pt, Cu, Zn, Fe, Ni), metal oxides (e.g., TiO_2, ZnO, CuO, Fe_xO_y), metal sulfides (e.g., CuS, Ag_2S, FeS), doped metal/metal oxides (e.g., Ag-TiO_2, Au-CuO, Pt-ZnO) and other metal-containing nanoparticles (quantum dots (QDs); e.g., $CdSe$, ZnS) can be classified as metallic nanoparticles[9-11].

Among metallic nanoparticles, silver nanoparticles (AgNPs) belong to the group of the most frequently used engineered nanomaterials (Fig. 1). This is a result of the well-documented antimicrobial properties of silver and the unique physicochemical properties of AgNPs, including high electrical and thermal conductivity [12]. The widespread range of applications of AgNPs in various consumer products, agriculture, medicine, (opto)electronics, the food industry, as well as many others, increases the chance of their elevated concentrations in the environment [8]. In this sense, AgNPs have become a contaminant of concern for the environment with the possibility of posing risks to human health [12,13].

Evidence that Ag ions can be easily released from AgNPs [14-18] and the ability of their acute toxic effects on the aquatic environments [19,20] has led to increased attention on their reliable quantification at ultratrace levels, particularly in aquatic matrices [9,21]. This challenge is usually achieved by using an efficient separation technique together with a reliable detection method. Among separation techniques, extractions have shown to be promising alternatives for their separation and preconcentration [22].

Depending on the extraction phase being used, a sample preparation procedure can be divided into solvent-based and sorption-based extraction. Sorption-based extraction techniques include solid phase extraction (SPE), dispersive solid phase extraction (dSPE), solid phase microextraction (SPME), stir bar sorptiveextraction

(SBSE), magnetic solid phase extraction (MSPE), thin-film microextraction (TFME), in-tube solid phase microextraction (IT-SPME), as well as several others [23].

Solvent-based extraction techniques include traditional liquid-liquid extraction (LLE). Its miniaturized form,so-called liquid phase microextraction (LPME) has three main variants depending of the separation mode used; single drop microextraction (SDME), dispersive liquid-liquid microextraction (DLLME), and membrane mediated liquid phase microextraction (such as hollow fiber liquid phase microextraction (HF-LPME) and solvent bar microextraction (SBME)) [24]. These techniques have many other modifications [25].A special modification of solvent-based extractions, where toxic organic solvents are replaced by nontoxic nonionic surfactants, so-called cloud point extraction (CPE) has also proven to be a promising option for separation/preconcentration of ENPs (including AgNPs).

This review aims to focus on the recent extraction techniques used for separation/preconcentration ofAgNPs in environmental matrices, especially in various water samples. Extraction techniques coupled with spectrometric methods, such as inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectrometry (ICP-OES), hydride generation atomic fluorescence spectrometry (HG-AFS), electrothermal atomic absorption spectrometry (ETAAS), flame atomic absorption spectrometry (FAAS), and UV/Vis spectrophotometry, will be mentioned in this paper.
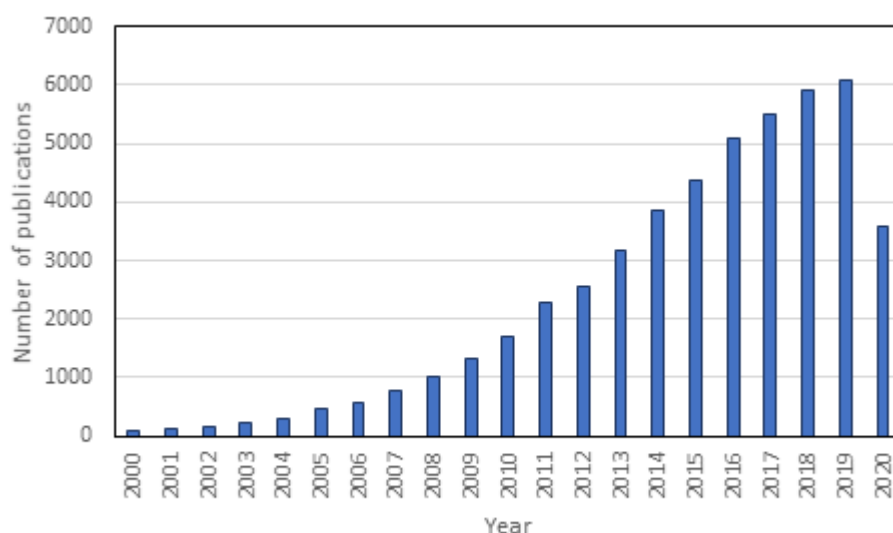

Fig. 1. Number of papers published on AgNPs.
(according to the Web of Science database; between January 2000-July 2020)

II. LIQUID-LIQUID EXTRACTION

In the past, traditional liquid-liquid extraction (LLE) was probably the most commonly used technique for separation of organic compounds as well as metal ions from various matrices. It is still sufficiently flexible technique to ensure isolation of a wide range of substances, but it requires the use of large amounts of potentially hazardous organic solvents [26]. In order to avoid this shortcoming, traditional LLE has undergone many modifications. The biggest one is the use of very small amounts of organic solvents (usually microliter volumes). In this case, we talk about liquid phase microextraction (LPME). In the literature, many subclasses of this technique with various modes and equipment are described. Some of them have also been used for the selective separation of AgNPs from environmental water samples.

A solvent microextraction where cyclohexane (volume of 150 μL) was used as the extractant for separation of citrate-stabilizedAgNPs, modified with mercaptocarboxylic acid,was described by Majedi et al. [27]. After optimization of experimental conditions, extraction recoveries in the range of 69.0–85.1% were achieved and the method was used for separation and preconcentration of AgNPs from tap and canal waters. Two spectrometric methods were used to quantify the analyte, namely ICP-OES and ICP-MS.

A typical dispersive liquid-liquid microextraction (DLLME) uses an extraction solvent mixed with a dispersive solvent and this solvent mixture is then rapidly injected into an aqueous sample. The rapid injection of the solvent mixture produces a cloudy solution. The formation of the cloudy solution allows for the instantaneous partitioning of analytes from the aqueous sample into the extraction phase [28]. An example of the use of a DDLE procedure for separation of AgNPs from natural waters and wastewaters can be found in the

paper published by Chen et al. [29]. They have usedionic liquid (IL), namely 1-octyl-3-methylimidazolium, as the extractant and methanol as the dispersion solvent. The extracted AgNPs in the IL phase were identified by transmission electron microscopy (TEM) and UV/Vis spectroscopy. Their quantification was done by ICP-MS.

Dispersive suspended microextraction (DSME) based on the dispersion of octanol into fine droplets was described by Choleva et al. [30]. In the first step, fine droplets of octanol were used for extraction of AgNPs from the bulk aqueous phase. Then, octanol was re-dispersed again in a strongly acidic and oxidizing aqueous medium (containing HNO_3 and H_2O_2) in order to selectively decompose AgNPs to silver ions. Finally, the aqueous extract was analyzed by FAAS. The developed method was suitable for separation of AgNPs of different size and coatings, thus enabling the quantification of the total AgNPs in real samples. It was demonstrated by analysis of natural waters as well as wastewaters.

In an effort to find out labile Ag^+ and total Ag^+ species in various sized AgNPsdispersions, a special kind of liquid extraction, namely hollow fiber supported liquid membrane (HFSLM), was developed by Chao et al. [31]. Silver ions in aqueous samples were extracted into the HFSLM made of tri-*n*-octylphosphine oxide in *n*-undecane, and stripped in the acceptor of $Na_2S_2O_3$ and $Cu(NO_3)_2$(prepared in phosphate buffer). After optimization, AgNPs were completely excluded by the liquid membrane and Ag^+ species were extracted into the liquid membrane with the help of TOPO carrier, and trapped in the acceptor through the exchange reaction with CuS_2O_3. This method is unique by the capability of distinguishing labile and total Ag^+ ions. It offers a new approach for evaluating the bioavailability and understanding the fate and toxicity of AgNPs in aquatic systems.

III. CLOUD POINT EXTRACTION

The use of neutrally charged surfactants (nonionic or zwitterionic) instead of hazardous organic solvents can be found in cloud point extraction (CPE) procedures. In this kind of extractions, an aqueous solution of a surfactant at a concentration higher than critical micellar concentration (CMC) becomes turbid and separates into two isotropic phases if an external condition is changed (e.g., temperature, pressure, pH, or ionic strength). The surfactant solution becomes turbid due to the incomplete solubilization [9]. At this point, the original surfactant solution separates into a surfactant phase of a small volume, which is rich in surfactant and contains an analyte trapped by micellar structures (so-called surfactant-rich phase; SRP) and a bulk diluted aqueous phase (so-called surfactant-poor phase or equilibrium solution) [32].

The potential to separate various nanoparticles (including AgNPs) by CPE was firstly shown by Liu et al.[33].In their later works, species-selective extractions of trace AgNPs in environmental waters and antibacterial products [34]and human hepatoma HepG2 celllysates [35] were outlined.They improved the phase separation by addition of $Na_2S_2O_3$. Moreover, $Na_2S_2O_3$ efficiently eliminated the interference of Ag^+ due to the complex formation between Ag^+ and $S_2O_3^{2-}$; such complex was not extracted into the SRP. After separation, AgNPs and Ag^+ contents were quantified by ICP-MS after microwave digestion of the two phases. Antibacterial products were also analyzed in the work published by Chao et al. [36]. They have applied a CPE procedure for speciation analysis of AgNPs and Ag^+ ions in six different commercial antibacterial products. Their results have shown that just three of them containedAgNPs.

Speciation analysis of AgNPs and Ag^+ carried out by two CPE procedures followed by ETAAS detection was described by López-García et al.[37]. One of them was realized in the presence and the other one in the absence of thiocyanate. A complex formed between Ag^+ and thiocyanate was not extracted into the SRP and thus, differentiation of the two species was reliable done. By using ETAAS for quantification, digestion of the SRP was not necessary and direct injection of the SRP into the electrothermal atomizer could be done. Finally, the methods were used to quantifyAgNPs in environmental waters, but also in lixiviates from sticking plasters and cleaning clothes [37]. An improved method for the quantification of AgNPs in environmental samples (such as river waters, treated and untreated wastewaters) by CPE and ETAAS was reported by Hartmann et al. [38]. Separation of AgNPs from their species was achieved by addition of ethylenediaminetetraacetate disodium salt (EDTA). In their later work [39], influence of particle coatings and matrix constituents on the CPE efficiency for AgNPs was studied. Thirteen types of AgNPs functionalized with environmentally relevant coatings (various organic and inorganic compounds as well as biomolecules) were compared and the effect of frequently occurring matrix constituents (various inorganic ions, natural organic matter, and colloids of TiO_2NPs) on the extraction efficiency was also investigated. From the tested coatings, just AgNPs functionalized with bovine serum albumin (which is a protein with the function to keep colloid in solution) were not extracted into the SRP. Extraction efficiencies in the range of 82−105% were achieved in the case of the other coatings studied.

IV. SOLID PHASE EXTRACTION

Solid phase extraction (SPE) is based on the analyte partition coefficient between the sample solution and the sorbent. In this technique, the sorbent is packed inside cartridges, syringe barrels, microcolumns, or disks.

An effective SPE method to selectively extract AuNPs, AgNPs and PdNPs from environmental waters (such as river, lake, andbrook) wasdescribed by Li et al. [40]. In the work, an ionic exchange resin (Amberlite IRN-78)which contains positively charged ammonium groups was used. The studied nanoparticlesmodified by mercaptosuccinic acid(MSA) were directly loaded onto the resin due to the electrostaticinteraction of the positively charged amino groups from theresin with the negatively charged carboxylic acid groups from theMSA ligands. In their later work [41], slight modification of the previously published SPE procedure was done and used for separation of AgNPs from wastewaters. Additionally, the concentration of AgNPs in effluent samples was also determined through a CPE method [38]. The determined concentrations of AgNPs in the field-collected effluents from nine municipal WWTPs were in the range of 2.2 to 9.4 ng/L using the SPE method, which was in good agreement with the results obtained by the CPE method.

A novel and versatile SPE device, namely a polytetrafluoroethylene (PTFE) knotted reactor (KR), was developed by Su et al. [42]. The device wasused to evaluate the biodistribution and dissolution behavior of intravenouslyadministered AgNPs in living rats. After optimization of experimental conditions, differentiation scheme for quantitative assessment of residual AgNPs and their released Ag^+ ions in complicated animal organs and tissues was worked out. Their results achieved have led to the conclusion that the administered AgNPs have been predominantly accumulated in the liver and spleen, with a gradual redistribution of Ag^+ ions to the kidney, lung, brain, and bloodstream.

The use of CdSe quantum dots (QDs) immobilized on a filter was described by Huang et al. [43]. Their method was based on a cation exchange reaction, occurred after injection of Ag^+ ions. In the case of AgNPs injection, no exchange was observed. Based on this principle, the simple speciation analysis of Ag^+ and AgNPs was conductedand quantification of Cd^{2+} released was done by hydride generation atomic fluorescence spectrometry (HG-AFS). The developed method was used to distinguish Ag^+ ions and AgNPs in antibacterial textiles and drugs.

Large pore mesoporous silica, modified with mercaptopropyl trimethoxysilane, was used to study adsorption of Ag^+ ions andAgNPsin the work published by Pongkitdachotiand Unob [44]. The material has shown to be an effective sorbent for the both species. Theiradsorption followed a pseudo-second order kinetic model, but the adsorption of Ag^+ ions took place more rapidly due to their much smaller size compared to AgNPs. Other finding of their study has led to the conclusion that the adsorption mechanism of the both species occurred via chemisorptionthrough the interaction with the thiol groups on the surface. The maximum adsorption capacity for Ag^+ ions and AgNPs was found to be 114.9 mg/g and 91.9 mg/g, respectively. Finally, the modified sorbent was used to adsorb the silver species from wastewater samples and spray samples.

The use of silica, modified with 3-aminopropyltriethoxysilane, was described by Anekthirakun and Imyim [45]. The adsorption behavior of Ag^+ ions and AgNPs was illustrated by the Langmuir model at 298 K. The maximum adsorption capacity of the modified sorbent for Ag^+ ions and AgNPs was 52.91 and 34.01 mg/g, respectively. Extraction of the both silver species from a binary mixture occurred rapidly within 5 min at the optimal pH 3. The selective desorption was also studied. It was successfully achieved by thiourea. Finally, the optimized method was applied to the determination of the silver species in various household products.

V. MAGNETIC SOLID PHASE EXTRACTION

Another alternative of SPE, named dispersive solid phase extraction (dSPE), is based on the addition of a solid sorbent to an agitated sample solution for a certain time. Afterwards, the suspension is usually centrifuged, and the sedimented sorbent with analytes is separated from the solution. Finally, a suitable solvent is used to elute the analytes from the sorbent before instrumental analysis.

There are various kinds of sorbents that can be used in dSPE methodology. In recent years, variety of nanomaterials have been preferred for use as potential sorbents in dSPE procedures for extraction of target analytes ina number of samples. Some of the critical aspects in this arrangement may be centrifugation and/or filtration. As a solution to this restriction, magnetic nanomaterials were proposed, since they perform phase separation more conveniently by the application of an external magnetic field. In this case, the method is named magnetic solid phase extraction (MSPE).

The application of unmodified and surface-modified magnetic particles in a MSPE procedure has been described by Mwilu et al. [46].Model analytes such as citrate-stabilized AgNPs and polyvinyl pyrolidone-stabilized AgNPs were used intheir study.In the presence of unmodified magnetic particles, selective removal of AgNPs in the presence of Ag^+ ions wascarried out. By using glutathione-functionalized magnetic particles and/or dopamine-functionalized magnetic particles, Ag^+ ions were partially coextracted along with AgNPs. Natural water samples spiked with AgNPs were applied in recovery studies to show the potential of their magnetic particles used for the separation and preconcentration of trace levels of AgNPs in real aqueous matrices.

The use of aged iron oxide magnetic particles (IOMPs) as MSPE adsorbents for speciation analysis of silver sulfide nanoparticles (Ag$_2$SNPs) was disclosed by Zhou et al. [47]. They found that IOMPs are

greatadsorbents for selective extraction of silver-containing nanoparticles (namely Ag_2SNPs, AgNPs, and AgClNPs) in the presence of Ag ions. A special finding that Ag_2SNPs can be distinguished from the other silver-containing nanoparticlesby sequential elution has ledto the validation of a method for speciation analysis of Ag_2SNPs in environmental water samples.

Magnetic chitosan microspheres as reusable adsorbents for selective separation of AgNPs in the presence of their ionic species have been prepared by Tolessa et al.[48].In their work, thorough study related to the effect of nanoparticle size and coating on the extraction efficiencies of AgNPs was done.The nanoparticles stabilized with citrate,polyvinyl pyrolidone, and polyvinylalcohol were extracted by the proposedprocedure with extraction efficiencieshigher than 91%. This means that their designed method has the application potential for separation/preconcentration of AgNPs stabilized with various capping agents with a similar functional group.

A method using poly(1-vinylimidazole) functionalized MNPs (PVIM-MNPs) for the adsorption of AgNPs and Ag^+ ionshas been described by Zhao et al. [49]. Usingmercaptosuccinic acid as a ligand exchanger, the both analytes were adsorbed on the PVIM-MNPs, and the sequential desorption of Ag^+ ions and AgNPs was reached by $Na_2S_2O_3$ and HNO_3, respectively. The coupling of ligand-assisted MSPE with ETAAS detection has led to the proposal of a procedure for the speciation of AgNPs and Ag^+ ions in environmental water samples.

VI. CONCLUSION

The extensive use of AgNPs increases the chance of their elevated concentrations in the environment. Thus, they are becoming emerging pollutants. They can enter to all environmental compartments. However, even in the aquatic environment, their behavior is not well understood and many questions about their fate remain unanswered. Their reliable quantification in real environmental matrices is the first step which can help to achieve a relevant information.

In the recent literature, increasing number of analytical techniques andmethods can be found for the quantification of AgNPs. Nevertheless, their application to complexmatrices is still very limited. It is due to the extremely low concentrations of AgNPs and complicated coexisting matrix. Among other things, the nanoparticles present a special kind of analytes, involving both chemical (namelycomposition, mass and number concentration) and physical information (namely size, shape, and aggregation)[7]. Moreover, information about the species derived from the nanoparticles themselves and their transformations should also be supplied. In this sense, the nanoparticles deserve a more comprehensive analytical approach. In some cases, a combination of really sophisticated methods, often very expensive, provides reliable results. The aim of this paper was to show the possibility to use well-established extraction techniques (such as LLE, CPE, SPE, and MSPE) in combination with commonly available spectrometric methods for separation/preconcentration and quantification of AgNPs in various environmental waters (including wastewaters). However, the great analytical potential of these combinations was also shown in the analysis of some antibacterial products and biological matrices. After optimization of experimental conditions, high preconcentration factors, quantitative recoveries, low limits of detection, and acceptable precision were achieved in most cases. This review demonstrates that a combination of extraction procedures and spectrometric methods can be considered as promising alternative for separation/preconcentration and quantification of AgNPsin real complex matrices.

ACKNOWLEDGEMENT

REFERENCES

[1]. Fernandes J.P., Mucha A.P., Francisco T., Rocha Gomes C., Almeida C.M.R. (2017) Silver nanoparticles uptake by salt marsh plants – implications for phytoremediation processes and effects in microbial community dynamics. Mar. Pollut. Bull. 119:176-183.

[2]. Ebrahimbabaie P., Meeinkuirt W., Pichtel J. (2020) Phytoremediation of engineered nanoparticles using aquatic plants: Mechanisms and practical feasibility. J. Environ. Sci. 93:151-163.

[3]. Suhendra E., Chang C.H., Hou W.C. (2020) A review on the environmental fate models for predicting the distribution of engineered nanomaterials in surface waters. Int. J. Mol. Sci. 21:4554.

[4]. Peng Z., Liu X., Zhang W., Zeng Z., Liu Z., Zhang C., Liu Y., Shao B., Liang Q., Tang W., YuanX. (2020) Advances in the application, toxicity and degradation of carbon nanomaterials in environment: A review. Environ. Int. 134:105298.

[5]. Romeo D., Salieri B., Hischier R., Nowack B., Wick P. (2020) An integrated pathway based on in vitro data for the human hazard assessment of nanomaterials. Environ. Int. 137:105505.

[6]. Šebesta M., Kolenčík M., Matúš P., Kořenková L. (2017) Transport and distribution of engineered nanoparticles in soils and sediments. Chem. Listy 111:322-328.

[7]. Laborda F., Bolea E., Cepría G., Gómez M.T., Jiménez M.S., Pérez-Arantegui J., Castillo J.R. (2016)Detection, characterization and quantification of inorganic engineered nanomaterials: A review of techniques and methodological approaches for the analysis of complex samples. Anal. Chim. Acta 904:10-32.

[8]. Šebesta M., Matúš P. (2018) Separation, determination and characterization of inorganic engineered nanoparticles in complex environmental samples. Chem. Listy 112: 583-589.

[9]. Hagarová I. (2017) Separation and quantification of metallic nanoparticles using cloud point extraction and spectrometric methods: A brief review of latest applications. Anal. Methods 9:3594-3601.

[10]. Majedi S.M., Lee H.K. (2016) Recent advances in the separation and quantification of metallic nanoparticles and ions in the environment. TrAC, Trends Anal. Chem. 75:183-196

[11]. Yaqoob A.A., Ahmad H., Parveen T., Ahmad A., Oves M., Ismail I.M.I., Qari A.H., Umar K., Mohamad Ibrahim M.N. (2020) Recent advances in metal decorated nanomaterials and their various biological applications: A review. Front. Chem. 8:341.

[12]. McGillicuddy E., Murray I., Kavanagh S., Morrison L., Fogarty A., Cormican M., Dockery P., Prendergast M., Rowan N., Morris D. (2017) Silver nanoparticles in the environment: sources, detection and ecotoxicology. Sci. Total Environ. 575:231-246.

[13]. López-Serrano A., Olivas R.M., Landaluze J.S., Cámara C. (2014) Nanoparticles: a global vision. Characterization, separation, and quantification methods. Potential environmental and health impact. Anal. Methods 6:38-56.

[14]. Kittler S., Greulich C., Diendorf J., Köller M., Epple M. (2010) Toxicity of silver nanoparticles increases during storage because of slow dissolution under release of silver ions. Chem. Mater. 22:4548-4554.

[15]. Ma R., Levard C., Marinakos S.M., Cheng Y., Liu J., Michel F.M., Brown G.E., Lowry G.V. (2011) Size-controlled dissolution of organic-coated silver nanoparticles. Environ. Sci. Technol. 46:752-759.

[16]. Dobias J., Bernier-Latmani R. (2013) Silver release from silver nanoparticles in natural waters. Environ. Sci. Technol. 47:4140-4146.

[17]. González-Álvarez R.J., Bellido-Milla D., Pinto J.J., Moreno C. (2018) Determination of silver in seawater by the direct analysis of solvent bars by high resolution continuum source solid sampling graphite furnace atomic absorption spectrometry. J. Anal. At. Spectrom. 33:1925-1931.

[18]. Wang X., Yang H., Li K., Xiang Y., Sha Y., Zhang M., Yuan X., Huang K. (2020) Recent developments of the speciation analysis methods for silver nanoparticles and silver ions based on atomic spectrometry. Appl. Spectrosc. Rev. 55:1-16.

[19]. Aghaei E., Alorro R.D., Encila A.N., Yoo K. (2017) Magnetic adsorbents for the recovery of precious metals from leach solutions and wastewater. Metals 7:529.

[20]. Zhao B., He M., Chen B., Hu B. (2018) Ligand-assisted magnetic solid phase extraction for fast speciation of silver nanoparticles and silver ions in environmental water.Talanta 183:268-275.

[21]. Liu J.F., Yu S.J., Yin Y.G., Chao J.B. (2012) Methods for separation, identification, characterization and quantification of silver nanoparticles. TrAC, Trends Anal. Chem. 33:95-106.

[22]. Wang X., Yang H., Li K., Xiang Y., Sha Y., Zhang M., Yuan X., Huang K. (2020) Recent developments of the speciation analysis methods for silver nanoparticles and silver ions based on atomic spectrometry. Appl. Spectrosc. Rev. 55:509-524.

[23]. Che D.D., Cheng J., Ji Z.Y., Zhang S.J., Li G.L., Sun Z.W., You J.M. (2017) Recent advances and applications of polydopamine-derived adsorbents for sample pretreatment. TrAC, Trends Anal. Chem. 97:1-14.

[24]. Ibrahim A.S.A., Al-Farawati R., Hawas U., Shaban Y. (2017) Recent microextraction techniques for determination and chemical speciation of selenium. Open Chem. 15:103-122.

[25]. Werner J., Grzeskowiak T., Zgola-Grzeskowiak A., Stanisz E. (2018) Recent trends in microextraction techniques used in determination of arsenic species. TrAC, Trends Anal. Chem. 105:121-136.

[26]. Gavazov K.B., Hagarová I., Halko R., Andruch V. (2019) Recent advances in the application of nanoparticles in cloud point extraction. J. Mol. Liq. 281:93-99.

[27]. Majedi S.M., Kelly B.C., Lee H.K. (2013) Efficient hydrophobization and solvent microextraction for determination of trace nano-sized silver and titanium dioxide in natural waters. Anal. Chim. Acta 789:47-57.

[28]. Quigley A., Cummins W., Connolly D. (2016)Dispersive liquid-liquid microextraction in the analysis ofmilk and dairy products: A review. J. Chem. 4040165.

[29]. Chen S., Sun Y., Chao J., Cheng L., Chen Y., Liu J. (2016) Dispersive liquid-liquid microextraction of silver nanoparticles in water using ionic liquid 1-octyl-3-methylimidazolium hexafluorophosphate. J. Environ. Sci. 41:211-217.

[30]. Choleva T.G., Tsogas G.Z., Giokas D.L. (2019) Determination of silver nanoparticles by atomic absorption spectrometry after dispersive suspended microextraction followed by oxidative dissolution back-extraction. Talanta 196:255-261.

[31]. Chao J.B., Zhou X.X., Shen M.H., Tan Z.Q., Liu R., Yu S.J., Wang X.W., Liu J.F. (2015) Speciation analysis of labile and total silver(I) in nanosilver dispersions and environmental waters by hollow fiber supported liquid membrane extraction. Environ. Sci. Technol. 49:14213-14220.

[32]. Hagarová I., Urík M. (2016) New approaches to the cloud point extraction: utilizable for separation and preconcentration of trace metals. Curr. Anal. Chem. 12:87-93.

[33]. Liu J.F., Liu R., Yin Y.G., Jiang G.B. (2009) Triton X-114 based cloud point extraction: a thermoreversible approach for separation/concentration and dispersion of nanomaterials in the aqueous phase. Chem. Commun. 12:1514-1516.

[34]. Liu J.F., Chao J.B., Liu R., Tan Z.Q., Yin Y.G., Wu Y., Jiang G.B. (2009) Cloud point extraction as an advantageous preconcentration approach for analysis of trace silver nanoparticles in environmental waters. Anal. Chem. 81:6496-6502.

[35]. Yu S.J., Chao J.B., Sun J., Yin Y.G., Liu J.F., Jiang G.B. (2013) Quantification of the uptake of silver nanoparticles and ions to HepG2 cells. Environ. Sci. Technol. 47:3268-3274.

[36]. Chao J.B., Liu J.F., Yu S.J., Feng Y.D., Tan Z.Q., Liu R., Yin Y.G. (2011) Speciation analysis of silver nanoparticles and silver ions in antibacterial products and environmental waters via cloud point extraction-based separation. Anal. Chem. 83:6875-6882.

[37]. López-García I., Vicente-Martínez Y., Hernández-Córdoba M. (2014) Speciation of silver nanoparticles and Ag(I) species using cloud point extraction followed by electrothermal atomic absorption spectrometry. Spectrochim. Acta, Part B 101:93-97.

[38]. Hartmann G., Hutterer C., Schuster M. (2013) Ultra-trace determination of silver nanoparticles in water samples using cloud point extraction and ETAAS. J. Anal. At. Spectrom. 28:567-572.

[39]. Hartmann G., Baumgartner T., Schuster M. (2014) Influence of particle coating and matrix constituents on the cloud point extraction efficiency of silver nanoparticles (Ag-NPs) and application for monitoring the formation of Ag-NPs from Ag^+. Anal. Chem. 86:790-796.

[40]. Li L., Leopold K., Schuster M. (2012) Effective and selective extraction of noble metal nanoparticles from environmental water through a noncovalent reversible reaction on an ionic exchange resin. Chem. Commun. 48:9165-9167.

[41]. Li L., Hartmann G., Döblinger M., Schuster M. (2013) Quantification of nanoscale silver particles removal and release from municipal wastewater treatment plants in Germany. Environ. Sci. Technol. 47:7317-7323.

[42]. Su C.K., Liu H.T., Hsia S.C., Sun Y.C. (2014) Quantitatively profiling the dissolution and redistribution of silver nanoparticles in living rats using a knotted reactor-based differentiation scheme. Anal. Chem. 86:8267-8274.

[43]. Huang K., Deng W., Dai R., Wang X., Xiong Q., Yuan Q., Jiang X., Yuan X., Xiong X. (2017) Ultrasensitive speciation analysis of silver ions and silver nanoparticles with a CdSe quantum dots immobilized filter by cation exchange reaction. Microchem. J. 135:74-80.

[44]. Pongkitdachoti U., Unob F. (2018) Simultaneous adsorption of silver nanoparticles and silver ions on large pore mesoporous silica. J. Environ. Chem. Eng. 6:596-603.

[45]. Anekthirakun P., Imyim A. (2019) Separation of silver ions and silver nanoparticles by silica based-solid phase extraction prior to ICP-OES determination. Microchem. J. 145:470-475.
[46]. Mwilu S.K., Siska E., Nasir Baig R.B., Varma R.S., Heithmar E., Rogers K.R. (2014) Separation and measurement of silver nanoparticles and silver ions using magnetic particles. Sci. Total Environ. 472:316-323.
[47]. Zhou X., Liu J., Chen Y., Yuan C. (2016) Speciation analysis of silver sulfide nanoparticles in environmental waters by magnetic solid-phase extraction coupled with ICP-MS. J. Anal. At. Spectrom. 31:2285-2292.
[48]. Tolessa T., Zhou X.X., Amde M., Liu J.F. (2017) Development of reusable magnetic chitosan microspheres adsorbent for selective extraction of trace level silver nanoparticles in environmental waters prior to ICP-MS analysis. Talanta 169:91-97.
[49]. Zhao B., He M., Chen B., Hu B. (2018) Ligand-assisted magnetic solid phase extraction for fast speciation of silver nanoparticles and silver ions in environmental water. Talanta 183:268-275.