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Spectrometric estimation of sample amount in aliquot for a direct solid sampling system and its application to the determination of trace impurities in silver nanoparticles by ETV-ICP-OES



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ABSTRACT

A method based on a tungsten boat furnace vaporiser, tungsten sample cuvettes, and an inductively coupled plasma (ICP) optical emission spectrometer has been developed for the direct determination of silicon, phosphorus, and sulphur in silver nanoparticles. The important point in the proposed method is that the entire sample in each batch is vaporised, which enables simultaneous measurement of the emission of not only the analyte but also the silver matrix. Furthermore, since the silver nanoparticles are sufficiently pure, the contribution of impurities to the sample amounts will be negligible. Therefore, this estimation is suitable for measuring the sample amount in each aliquot instead of the conventional weighing procedure using a microbalance; therefore, no tedious weighing procedures for estimating the sample amount introduced into the ETV device are needed. An additional advantage is that pretreatment and/or predigestion are unnecessary. The sample throughput is approximately 35 batches per hour. The detection limits of silicon, phosphorus, and sulphur in the silver nanoparticles (dry powder) are 15, 4.2, and 62 $\mu\text{g g}^{-1}$, respectively. Analytical results for various silver nanoparticles as both dry particles and in suspended solutions are described, and these values are compared to those obtained by conventional weighing with a microbalance. This methodology is useful for rapid screening and accurate analysis of silver nanoparticles, especially for industrial applications.

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1. Introduction

As membrane wiring boards and flexible printed circuits have increasingly been developed and fabricated, electronic applications, especially for domestic use, have become progressively sophisticated. Among electronic parts, transparent electrodes are essential components because they are used daily in the touch panels of smart and cellular phones, LED screens and plasma display panels, solar cell electrodes, and, recently, wearable computers; in addition, there are a variety of future applications. These transparent electrodes are sometimes produced by painting a gel-ink or a paste of a certain conductive material on transparent, flexible sheets. During aging of the sheets, the nanoparticles aggregate to form numerous narrow wires, similar to knitting. Light

Abbreviations: ICP, inductively coupled plasma; ETV, electrothermal vaporisation; OES, optical emission spectrometry; GF-AAS, graphite furnace atomic absorption spectrometry; MS, mass spectrometry; TBF, tungsten boat furnace; CRM, certified reference material; EPMA, electron probe microanalyser

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transmits through the many openings among the wires. The conductive materials are prepared by suspending nanoparticles in aqueous or organic solvents. Gold, silver, copper, iron, nickel, etc., and their alloys are used as the nanoparticles. Gold and platinum have excellent durabilities, although they are also the most expensive. Hence, they have been applied primarily in biological and medical areas, where the research can be performed using a small amount of nanoparticles. Copper particles can be purchased at lower prices; however, they are not as durable. Silver particles have a higher durability and are more cost-effective than other metals. Therefore, in industry, silver nanoparticles have been applied comprehensively. In the industrial process for producing silver nanoparticles, there are impurities, which negatively influence the quality of the final products by affecting the dispersibility, printing properties, and storage stability in the liquidised suspended solution form; these impurities include sulphur, silicon, and phosphorus. Even in the metallic solid form, the conductivity of the silver nanoparticles is seriously affected by impurities, and the influence of the impurities is often observed at very low concentrations. For example, the dispersibility deteriorates with increasing concentration of silicon even when sufficient amounts

of surfactant are present as a dispersing agent ([Supplementary material; Data_1.PDF](#)). Sulphur pollution of raw materials can also impede the electronic conductivity of the final products or transparent electrodes ([Supplementary material, Data_2.PDF](#)).

The development of a rapid and facile analytical method for the determination of impurities in silver nanoparticles as industrial materials is necessary. For determining these impurities in silver nanoparticles, inductively coupled plasma optical emission spectrometry (ICP-OES) is a powerful tool from the perspective of satisfactory stability, good repeatability, wide calibration range, and sufficient sensitivity. Depending on the analyte impurities, e.g. metallic elements, it is considered feasible that the silver nanoparticles could be dissolved in nitric acid and then analysed for impurities with nebuliser ICP-OES. However, for the determination of silicon, phosphorus, and sulphur, there is a risk that the silicon impurities will precipitate as silicic acid under such strongly acidic conditions during the final digest. Sulphur and phosphorus often evaporate during vigorous digestion procedures. Moreover, the digestion procedures are usually tedious, time-consuming, and besides, the analytes tend to be contaminated by the laboratory conditions. For sample introduction, although pneumatic nebulisation has been widely applied, direct solid sample introduction schemes are attractive from the viewpoint of analysing only small amounts (several milligrams) of samples, avoiding the contamination inherent to sample preparation procedures, and reducing the time required by avoiding dissolution, dilution, and filling steps. Moore et al. and Sarah et al. applied the laser ablation technique to the direct analysis of ancient or antique silver products [1,2]. An alternate direct introduction technique for solid samples into ICP, i.e. the electrothermal vaporisation (ETV) sample introduction technique, is applicable to solid samples as well as liquid or suspended solutions. Moore and co-workers [3] reported a unique ETV technique based on one-particle sampling followed by *in situ* digestion with nitric acid in a graphite tube furnace. According to their paper, the matrix silver and almost all the analytes dissolved completely to form their nitrate salts, with impurities, such as tin, precipitating in the furnace. The concept was that, regardless of their solubility, all the elements were converted to a species that was suitable for electrothermal vaporisation. In the case of silver nanoparticles, the sample diameter is too small and too little sample is required to accurately and reproducibly weigh aliquots of the particles and place them into the furnace. If the silver nanoparticles were suspended in aqueous or organic solvent in the presence of a suitable surfactant via ultrasonication, the particles would precipitate rapidly because of their high density relative to the solvent. Indeed only several seconds are sufficient for sedimentation ([Supplementary material, Data_3.PDF](#)). Even if a stable suspension were prepared, the particles would be too hydrophobic to pipette and inject them accurately without some remaining inside the wall of the pipette ([Supplementary material, Data_4.MP4](#)). With respect to the practicality, there are some handicaps regarding the operation of the ETV-ICP-OES, i.e. estimation of the amount of silver nanoparticles, quantitative introduction of the particles into the ETV device, and the tedious removal of residues if necessary. In particular, estimating the amount of each aliquot taken is the most significant problem in solid sampling ETV because dividing the amount of impurities by the weight of aliquot is necessary to calculate the concentration. When the applied amounts are in the range of several tens of milligrams to sub-gram, the samples can be easily weighed via the usual microbalance procedure by using an exchangeable sample cuvette-tungsten boat furnace system [4]. However, when each aliquot is only several milligrams, the weighing procedure is difficult because of the insufficient sensitivity of the microbalance.

Since the original ICP-OES method is used for the

determination of ultratrace impurities, ICP-OES incorporating an ETV device enables further detectability. Therefore, the method is not generally suitable for the quantification of major components. By utilising a wavelength with poorer sensitivity, however, the dynamic range for calibration can be expanded to higher concentrations. In this paper, the entire sample in each batch is vaporised for introduction into the ICP emission source, and both the emission intensities of the analyte and matrix silver are measured simultaneously at their respective wavelengths using a spectrometer incorporated two independent monochromators. That is, in order to measure the sample amount in each batch, a spectrometric estimation was applied instead of the conventional weighing method involving a microbalance; concurrently, the analyte impurities are determined by the other monochromator.

With respect to nanoparticles, significant attention is devoted to counting individual nanoparticles in environmental samples to evaluate pollution by metal particles.

To the best of our knowledge, the trace determination of silicon, phosphorus, and sulphur impurities in silver nanoparticles has not been reported to date. There are only reports regarding the determination of free Ag^+ ions as an impurity in a silver nanoparticle solution by fluorescence spectrometry [5] and ICP mass spectrometry (MS) [6]. A direct solid sampling scheme was applied to the determination of silver nanoparticles themselves in botanical samples by high-resolution continuum source GF-AAS [7]. Buchbinder et al. reported the application of a separate sampling and excitation accessory for ICP-OES for the direct analysis of silver ingot [8]. Yang et al. developed a method to isolate trace metal impurities from a silver matrix using selective precipitation followed by ICP-MS [9] and neutron activation analysis [10]. However, although there is potential for the determination of silicon, phosphorus, and sulphur using these methods, no data concerning these elements were reported. Regarding the determination of silicon, phosphorus, and sulphur, Jiang and co-worker reported the determination of these elements in steel samples using ICP-MS [11]. However, silver samples were not investigated.

2. Materials and methods

2.1. Reagents

Water from an Advantec Toyo (Tokyo, Japan) Model GSU-601 water purification system was used. All chemicals were commercially available and of analytical reagent grade. Stock standard solutions (1000 mg L^{-1}) of sulphur and phosphorus were prepared by dissolving potassium sulphate and anhydrous potassium dihydrogenphosphate, respectively, in water. Working solutions were freshly prepared by diluting appropriate aliquots of the stock solutions or previously diluted solutions with water. Stock solutions containing $10,000$ and 1000 mg L^{-1} silver(I) were purchased from Hayashi Pure Chemical (Osaka, Japan). Standard silicon(IV) solutions with concentrations of 10 and 100 mg L^{-1} were purchased from Hayashi Pure Chemical and used as received with no further dilution. Small circular silver pieces were prepared by cutting highly purified silver thin plate (0.01 mm thickness, 99.98% , Nilaco, Tokyo, Japan) into circles with diameters of 0.8 mm and masses of approximately 60 mg .

2.2. Silver nanoparticles

Dry particles of silver nanoparticles were purchased from Tanaka Kikinzoku Kogyo (Tokyo, Japan). Other silver nanoparticles were prepared according to the literature [12]. Briefly, into a litre aliquot of 10% silver nitrate aqueous solution containing 3.6 g of Disperbyk-190 (BYK Japan, Tokyo, Japan) as a dispersing agent,

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