# Detection of Nanosilver Agents in Antibacterial Textiles

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**Abstract.** The analytical techniques are needed to detect the nanosilver in textiles in direct contact with skin. In this paper, in order to discuss the extraction of nanosilver on the surface of textiles by human skin, we demonstrate the capability of constant temperature oscillation extraction method followed by Inductively Coupled Plasma Spectroscopy (ICP). The sweat and deionized water were selected as extraction solvent simulating the contact process of human skin with textiles. The SEM and TEM analysis shows the existence of nanosilver in the fabric and aqueous extract. ICP analysis shows accurately when analysing silver amounts in the range of 0.05~1.2 mg/L with $r^2$ values of 0.9997. The percent recoveries of all fabrics were all lower than 44 %.The results shows that the developed method of simulating of human sweat extraction was not very effective. So the nanosilver might not be transferred to human body effectively from the fabric.

## 1. Introduction

Nanoparticles are commonly used in commercial products in the range of 1-100 nm [1], which has unique physical and chemical properties different from bulk materials based on specific characteristics, such as size, distribution, and morphology [2]. Nanosilver is one of the most studied nanomaterials. For instance, silver nanoparticles are increasingly added to daily consumer goods because silver nanoparticles have a high biocidal effect against bacteria, viruses and fungi [3]. Known for its antibacterial properties, nanosliver also acts as an effective agent for destroying a wide range of Gram-negative and Gram-positive bacteria [4]. In addition, the specific surface area of silver nanoparticles can reach several 100 $m^2/g$. Their specific surface properties enrich silver nanoparticles with unusual physicochemical properties quite different from those typical of solid materials [5].

The increase in the usage of nanosliver in daily products leads to growing concens about the safety of nanosliver to humans and the environment. A large number of studies have been conducted and are being performed to assess the risks of nanosliver in the environment and food to human and ecological health [6]. Stebounova's group studied the effects of inhaled nanosilver in mice. Nanosilver was present in the air at a concentration of 0.0033 $mg/dm^3$ and the average size of nanosilver agents was about 10 nm. In the exposure chamber, the mice breathed the air for 4 h per day. After 10 days the studies revealed that nanosilver could not be degraded by organisms, and it can accumulate in the lungs of mice. The studies also observed that exposing mice to the nanosilver-containing air induced pulmonary inflammation [7]. Sung's groop also conducted a similar study. It was concluded that with increasing concentrations of nanosilver, the lung atrophy was also increased. It was also noted that some changes in the physical appearance of the other organ [8]. After reviewing the correlation studies, we find that nanosilver is not only poisonous, but also can accumulate in the human body.

The widespread use of nanosilver in textiles means it could pass through the dermis layer of body skin and enter the blood circulation system. So it could be deposited in all parts of the body. The accumulation of nanosilver in the organ may also cause negative effects that can be reflected in the future.

In this study, we would detect the nanosilver which has potential threat to the human body from antibacterial textiles. Fabrics were used for antibacterial finishing with nanosilver solution. The total amount of silver was determined by microwave digestion method followed inductively coupled plasma (ICP) method. The efficiency of water extraction and simulated acid sweat extraction were compared, which would help us to discuss the extraction of nanosilver on the surface of textiles by human body. Then the nanosilver particle size of the extract was characterized, which would help us to discuss the potential toxicity of antibacterial textiles to the human body.

## 2. Experimental

### *2.1. Materials and Instruments*

The colorless and transparent nanosilver aqueous solution (5 nm, 2000 ppm) was purchased from Yurui Corporation (Shanghai, China). Concentrated nitric acid, NaOH, $NaH_2PO_4$ and NaCl with analytical grade were purchased from Beijing Reagent Company (Beijing, China). L-histidine monohydrate (99 %) was purchased from J&K Chemical Company (Beijing, China). Standard silver solution (1000 μg/mL, 50 mL) was purchased from China National Institute of Metrology (Beijing, China). MU504A Padder was purchased from Beijing Institute of Textile Machinery and Equipment (Beijing, China), 907511 Microwave Digestion Instrument was purchased from CEM Corporation (Japan, Tokyo), Spectro Ciros Inductively Coupled Plasma was purchased from Spector Corporation (Germany), JEM-7500F Scanning Electron Microscope was purchased from JEOL Corporation (Tokyo, Japan), HT7700 Transmission Electron Microscope was purchased from HITACHI Corporation (Tokyo, Japan,), SHZ-28A Constant Temperature Water Bath was purchased from Huamei Corporation (Taicang ,China), KQ5200DE Ultrasonic Cleaner were purchased from Yuhua Instrument Corporation (Gongyi ,China).

### *2.2. Fabric Scouring and Finshing*

Pure cotton fabrics were scoured by 5 % NaOH in the condition of bath ratio 1:30 in an water bath at 100 °C for 1 h. Cotton-polyester blended fabrics were scoured by less than 1 % NaOH in the condition of bath ratio 1:30 in an water bath at 60 °C for 1 h.

2000 ppm of nanosilver solution was diluted with distilled water to 10, 30, 60 mg/L solution. Before using of concentrated solution, the nanosilver solution was treated by ultrasonication three times to ensure uniform dispersion of nanosilver. Pure cotton fabric and cotton-polyester blended fabric were dipped in dilution solution of nanosilver (50 ℃, 30min) at the bath ratio of 1:30, and then the finishing process were two dipping and two rolling. After finishing process, the fabrics were dried naturally at room temperature. The finished fabrics were washed thoroughly with water to remove free nanosilver before detection.

### *2.3. Preparation of Analytical Sample*

A microwave digestion method was applied in sample preparation using a hermetically-sealed polytetrafluoroethylene (PTFE) digestion tank [9]. A dosage of 0.1g (accurate to 0.0001g) antibacterial fabric was cut as close to the scalp as possible and was added into PTFE digestion tank, then 9 mL concentrated nitric acid was added. The programme of digestion was as follows: the initial temperature was 30 °C, 9 °C/ min to 120 °C (5 min), 4 °C/ min to 160 °C (10 min), 2 °C/ min to 180 °C (20 min). An overall time was 65 min. At the same time, the blank experiment of pure acid and pure acid added in blank fabric were conducted. Then the digestion solution was diluted to a 50 mL volumetric flask prior to ICP analysis.

Antibacterial fabrics which prepared according to above method (2.2) were cut as close to the scalp as possible and were stored in a 100 mL conical flask. The sweat and water were selected as extraction solvent. According to the published methods, samples could be extracted by constant temperature

oscillation, ultrasonic assisted extraction and soxhlet extraction [10]. The efficiencies of three extraction methods were compared using parallel samples. The optimal extraction conditions were as follows: 2.0 g (accurate to 0.001g) of ground sample was placed into a 100 mL conical flask, and then 40 mL deionized water was added. Then, the flask was immersed in a water bath at 37 ± 2 °C for 1 h with the speed of 90 r/min. The final extract was diluted to a 100 mL volumetric flask prior to ICP analysis. Blank experiment was done at the same time. According to the composition of sweat [11], the 1000 ml simulated sweat was composed with 0.5g L-histidine monohydrate, 5.0g NaCl, 2.2g monometallic sodium orthophosphate aqueous solution, and pH was adjusted to 5.5 ± 0.2 by 0.1 mol/L NaOH. The extractive solution was also observed by HT7700 Transmission Electron Microscope (TEM).

### *2.4. Scanning Electron Microscopy (SEM), Transmission Electron Microscope (TEM) and ICP Analysis*

SEM imaging was performed using JEM-7500F Scanning Electron Microscope at 5.0 kV acceleration voltage and at a 8.3 mm working distance. The scanning electron microscope samples were the fabric before and after finishing. TEM images were acquired by a HT7700 Transmission Electron Microscope (80 kV). The extraction solution should be treated by ultrasonication before TEM detection to make the nanosilver particle dispersed. The ultrasonic liquid samples were then applied to the clean copper grids, which were dried naturally at room temperature for TEM use.

The concentration of nanosilver was determined on Spectro Ciros Inductively Coupled Plasma (ICP). The operating conditions were as follows: ICP Radio Frequency Power: 1350 W; Nebulizer Gas flow: 1 L/min; Auxiliary Gas flow: 1 L/min; Plasma Gas Flow: 12 L/min; Wavelength: 328.068 nm. The operating conditions were optimized daily by using an aqueous solution containing 1 mg/L of Ag with precision better than 2%. The standard solutions of 0.05, 0.2, 0.4, 0.6, 0.8, 1, and 1.2 mg/L were prepared by diluting the standard silver solution (1000 μg/mL) in the 100 mL volumetric flask. The standard curve was plotted with ICP.

## 3. Results and Discussion

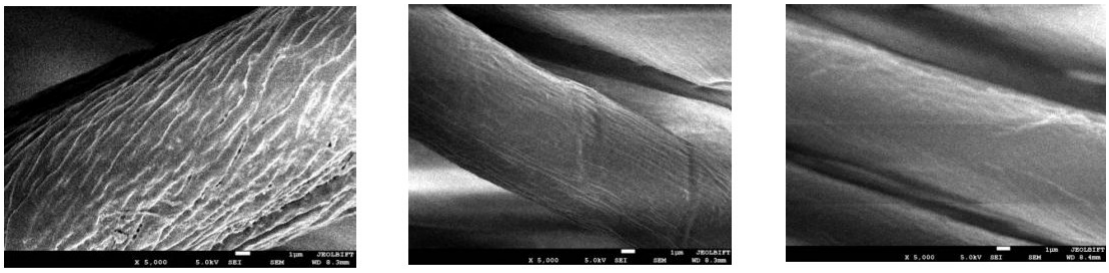
### *3.1. Conditions of Scouring and Finshing*

Pure cotton fabric with more impurities has great resistance to alkali, so the scouring condition for pure cotton fabric was 5 % NaOH at 100 °C water bath. But polyester-cotton blended fabric has a bad alkali resistance and temperature resistance, so it was scoured by less than 1 % NaOH at 60 °C water bath [12].

In finishing process, dipping at higher temperature with long time was beneficial to the adsorption of nanoscale silver on fabric. But the temperatures over 60 °C will make nanosilver reunite on the surface of the fabric. The smaller bath ratio would cause the uneven distribution of nanosilver, and the larger bath ratio would cause waste. It is decided to use the condition of 50 °C with the bath ratio of 1:30. After finishing process, the fabrics were dried naturally at room temperature to avoid decreasing whiteness at higher temperature.

### *3.2. Scanning Electron Microscope of finished fabric*

The SEM was used to observe the blank fabric and the finished fabric. Nanosilver was added to fabrics under finishing process to provide antibacterial performance of textiles. These three graphs (Fig.1) are under the same magnification. There are some differences in the three pictures. It can be clearly seen that the surface of the fiber finished by nanosilver solution becomes rough although it is not possible to see the nanosilver particles on the surface. It can be roughly judged by surface morphology that nanosilver was distributed on the surface of fiber. So we can infer from the SEM that the nanosilver is directly in contact with the human body when wearing nanosilver fabrics. So nanosilver might be extracted by sweat and absorbed by the body.



（a）×5000 （b）×5000 （c）×5000

**Figure 1.** Microscopic images of cotton fiber: (a) surface of not modified; (b) 1 mg/L nanosilver modified fibers; (c) 10 mg/L nanosilver modified fibers.

*3.3. Selection of Extraction Methods*

The efficiencies of three extraction methods were compared using parallel samples. To avoid accidental results, in the experiments we adopted the antibacterial fabric which finished with 20 mg/L and 60 mg/L nanosilver solution. The results are displayed in Fig.2.

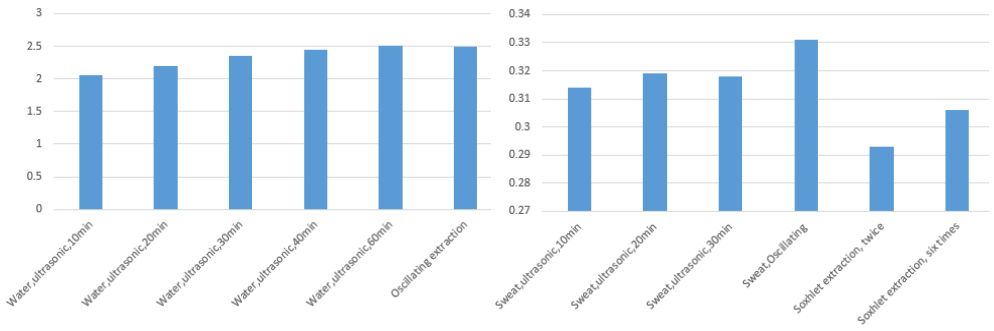



**Figure 2.** Extraction efficiency of different extraction methods

It can be seen from the Fig.2 that the extraction efficiency of constant temperature oscillation was the best. The extraction condition of constant temperature oscillation was very similar to the human body, so we can conclude that the extraction of nanoscale silver by human sweat should be better than other extraction methods. But the experimental results showed that water was more superiority than sweat (Fig. 3). We deduced that the sweat from the skin would be not conducive to the extraction of nanosilver. Moreover, the extraction efficiency of ultrasonic extraction was equivalent to constant temperature oscillation using water as solvent with longer ultrasonic time.

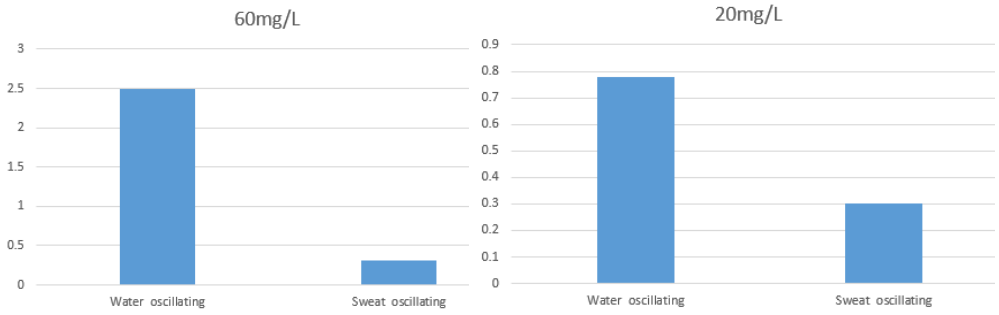
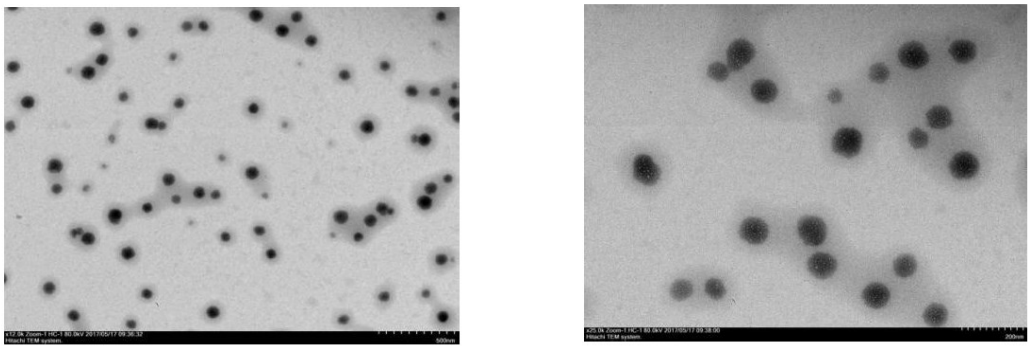



**Figure 3.** Extraction efficiency of different solvents

The TEM was used to observe the size of nanosilver in extraction solution. From the TEM photos (Fig. 4), we could see that nanosilver existed in the nanoscale and evenly dispersed in the solution.

The particle morphology was spherical, and particles had no obvious agglomeration. The particle size was about 40-70nm. So we could deduce that the nanosilver extracted by human sweat might penetrate the skin of human body and accumulate in the human organ.



（a）×12k （b）×25k

**Figure 4.** TEM photos of extraction solution at 12k, 25k amplified factor

*3.4. Working Curve and Recovery*

According to the procedure, the overall concentrations of silver in different fabric (cotton fabric and cotton-polyester blended fabric) which were finished with three nanosilver solutions (10 mg/L, 30 mg/L and 60 mg/L) were measured by ICP after microwave digestion, and the corresponding concentrations of aqueous extract were also determined by ICP. The Working Curve of the silver standard solutions was measured. The standard curve was Y = 306612 X - 1011.2, and the correlation coefficients ($r^2$) exceeded 0.999. The percent recoveries were displayed in Table 1.

**Table 1.** The percent recovery

| Samples | Concentration of finishing solution(mg/L) | The percent recovery |
|---|---|---|
| cotton fabric | 10 | 12.01% |
| | 30 | 31.83% |
| | 60 | 43.01% |
| cotton-polyester blended fabric | 10 | 17.22% |
| | 30 | 26.10% |
| | 60 | 39.60% |

The percent recovery = (silver amount of aqueous extract) / (total silver amount). It is shown in Table 1 that the percent recoveries of all fabrics were all lower than 44 %. The low percent recovery showed that the developed method of simulating of human sweat extraction was not very effective. So the nanosilver might not be transferred to human body effectively from the fabric.

## 4. Conclusions

In this study, the determination of trace amounts of nonosilver in textiles which has potential threat to the human body was developed. The nanosilver fabrics were prepared by two dipping and two rolling process with nanosilver solution. Constant temperature oscillation extraction method was developed by comparing the extraction efficiency of sweat and deionized water. The SEM and TEM analysis showed detail information about the existence of nanosilver in the fabric and aqueous extract. ICP analysis showed accurately when analysing silver amounts in the range of 0.05 ~ 1.2 mg/L with $r^2$ values of 0.9997. The percent recoveries of all fabrics were all lower than 44 %. Therefore, the

proposed method simulating of human sweat extraction was not very effective. Otherwise, the nanosilver might not be transferred to human body effectively from the fabric.

## 5. Acknowledgements

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