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Zinc Nanoparticles Effect on the Parameters of Water

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Abstract. **The article is associated with the detection of metal nanoparticles concentration in water. The main risks associated with the metal covered textile use are metal nanoparticle separation from material in use and maintenance processes, resulting in a threat to living organisms. This article aims to look at options to recognize the presence of zinc oxide nanoparticles in water, applying the GDV electrography method and by analyzing parameters of electrogrammes, distinguish those who respond to the presence of particles and their concentration changes.**

***Keywords*: electrography, GDV parameters, metal covered textile, zinc nanoparticles.**

I. Introduction

In recent years the range of different metal nanoparticle applications in form of finish / components / coatings hve increased rapidly, including cosmetic products, clothes and household applications. Nano-scale modifications offer protection from UV rays, remove unpleasant odor agents (microorganisms) in assortment of sleepwear and hosiery, household fabrics, provide antibacterial effects of dental care products and washing machines. Introduction of new properties into products of traditional-use has to be support by confidence that nano-scale modifications will not cause irreversible changes in living and working environments during manufacturing and usage. Nano-scale particles as opposed to substance, from which they come, are very active and released into the environment, including air and waste water, can cause serious problems, which consequences must be taken into account making product design, manufacturing, using and removing [1].

The main risks associated with the use of metal covered textile are the separation of metal nanoparticles. Nanoparticles can be detached from the product in result of friction during manufacturing and usage processes, resulting in pollution of environment, or inhaled by humans or animals. Nanoparticles can also be detached from the textile in the washing processes, thereby contaminating the sewages and exterminate useful bacterium, causing detriment to other inhabitants of water reservoirs as despite of the positive properties of metal coverings (antibacterial, fungicidal, analgesic, blood circulation-improving effect) in small quantities, large quantities of metal nanoparticles can cause toxicosis and pollute the environment. Results of intensive studies carried out to investigate influences of metal nanoparticles on humans and environment show that metal nanoparticles / ions destroy species of bacteria in sewage purifying systems [1] and introduced into mammalian cells, aggressive nanoparticles / ions can cause damage to genotype [2].

The article analyzes the issues related to the stability of metal nanolevel coatings of textile during cleaning, paying special attention to researches on the possibilities to identify zinc nanoparticles presence and concentration in the effluent. Detection of metal nanoparticles in fluids based on the principles of gas discharge visualization provides a valuable method for the perspective solution. In the study discharge visualization device (GDV camera) and accessories for liquid analysis have been used.

II. Devices for Detection and Characterization of Nanoparticles

Quantitative assessment of the impact of nanoparticles and adequate characterization provides a serious problem for scientists, industrial hygienists and toxicologists. Nanoparticle dimensions are outside the visible light diffraction limit, thus in the optical microscope they are not visible, which creates a need for highly sensitive testing method.

There is a number of equipment for nanoparticle detection, measurement and characterization in liquids, gases and solids [3].

None of the methods can be considered universal or best, choice of method is determined by many factors, including sample type, the required amount of information, time constraints and costs. Depending on the selected equipment such information as number of nanoparticles, their weight, size, size distribution, surface area could be obtained, or presence of nanoparticles in a given sample recognized. This type of equipment can be regarded as measuring equipment. There is also a facility for characterization of nanoparticle chemical structure, which allows estimating the sample composition, reactions on the surface of nanoparticles or their interaction with other sample components. This type of equipment varies whether the nanoparticle clusters or single nanoparticles are analyzed [4].

Some equipment requires prior sample preparation, but there are also such devices, which can measure crude substance [5]. The required pre-treatment is problematic because the sample in preparation process can react or decompose. Testing required quantity of the substance can limit the choice of equipment, because, depending on the equipment, requires more than 1 mg [4].

When testing liquids with GDV camera, the pre-treatment of sample is not needed, and the size of the sample required for the analysis can be reduced to a few drops. Dynamic Electrophotonic Capture (EPC) method, implemented by GDV camera, is based on the stimulation of photon and electron emissions from the surface of the object whilst transmitting short electrical impulses. Emitted particles accelerate in the electromagnetic field, generating electronic avalanches on the surface of the dielectric (“sliding gas discharge”). The discharge causes glow due to the excitement of molecules in the surrounding gas, and this glow is measured by the EPC method. When the EPC parameters are measured for liquid subjects, a drop of the liquid is suspended at 2-3 mm distance above the glass surface of the optical window of the device. The train of triangular bipolar electrical impulses of amplitude 3 kV at a repetition frequency of 103 Hz, is applied to the conductive transparent layer at the back side of the quartz electrode thus generating an electromagnetic field at the surface of the electrode and around the drop. Under the influence of this field, the drop produces a burst of electron-ion emissions and optical radiation light quanta in the visual and ultraviolet light regions of the electromagnetic spectrum. A spatial distribution of discharge channels is registered through a glass electrode by the optical system with a charge coupled device camera. High-frequency high-voltage current produced discharge or radiation around an object is detected by a digital camera in separate shots or video format. Radiation shape and size reflect the object properties. The resulting images are analyzed by specialized software [6; **7**].

Nanoparticles detection equipment is suitable for environment in which particles are detected – fluid, air or solid. It should be noted that airborne nanoparticles may be the result of the liquid aerosol spray - nanoparticles with small particles of liquid substances - or had elevated up in the air by pyrolysis or other chemical or physical process. Nanoparticle detection methods and devices may also be classified according to the parameters they can calculate, such as mass concentration, number of the particles (numerical concentration), specific of the surface (surface concentration) or granulometric structure. Equipment connected to a computer (on-line) or equipment without connection to computer (off-line) could be used [8].

Methods which are used to detect nanoparticles in water are based on the microscopy method, by using such microscope types as Transmission Electron Microscope (TEM), Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM). For nanoparticles analysis Brown's motion-based equipment - Photon Correlation Spectroscopy and Nanoparticle Tracking Analyzer- are often used too.

The above mentioned methods differ in the required sample size for measurements, the preparation techniques and the resulting parameter range. Microscopy techniques are time consuming; their realization requires expensive equipment and skilled technical staff resulting in high testing costs. The necessary pre-treatment is problematic as well, because the sample may react or decompose during the preparation. Photon Correlation Spectroscopy requires additional measurements to calculate the indicators.

Most of mentioned before equipments and methods cannot distinguish between the individual nanoparticles and agglomerates of nanoparticles, which limits their use because toxicity of nanoparticles depends on their size - the size reduction increases toxicity (Fig. 1). Both the toxicity of nanoparticle agglomerates and the particular individual nanoparticle are greater than the equivalent-sized whole substance toxicity.

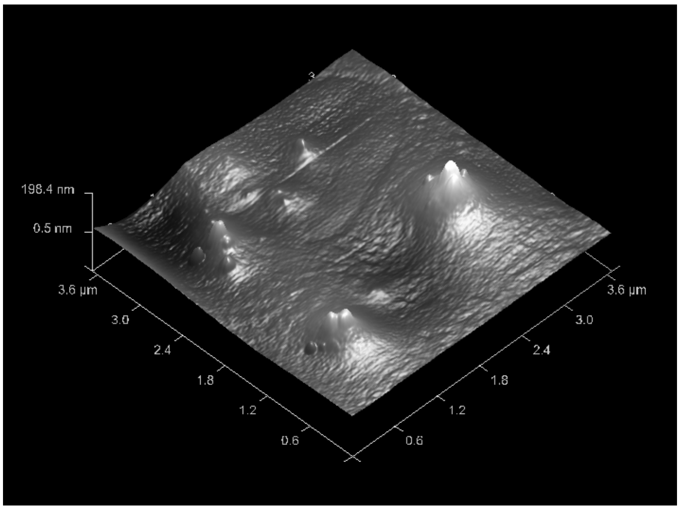


Fig.1. In experiment used Zn nanoparticles and their agglomerates fixation in AFM micrograph.

Electrography based on GDV equipment is a comparative method, namely standard is needed to compare the results. Analyzing the water, as the standart most commonly distilled water is used, as has been done in this experiment.

III. RESEARCH METHODOLOGY

To make sure that electrogramme parameters reflect nano-scale metal particles / ions present in the water, the deliberately contaminated distilled water with zinc nanoparticles has been used. In three distilled water samples (6 ml each) zinc oxide nanoparticle (average horizontal size 60 nm, vertical 30 nm) powder was added: 1 Zn sample 0.09 g; 2 Zn sample 0.06 g; 3 Zn sample 0.03 g. The result is the following concentration for each sample:

1 Zn - 1.5%;
2 Zn - 1.0%;
3 Zn - 0.5%.

Polluted and unpolluted water were stored in locked containers. Before electrography session bowl with water is shaked thoroughly to disperse the sludge. Prepared water (0.2 ml) was embroiled into a syringe and a syringe fixed on a stand above the GDV camera lens. From the same sample 5 GDV static electrogrammes have been obtained. The experiment was repeated eight times, resulting of the 40 files with the same time interval between electrogrammes fixing moments. Equipment test results [9] showed that sufficiently reliable data was needed to obtain at least 40 measurements per experimental subject. Time intervals between the electrogrammes fixation moments 3, 5 and 7 seconds are applied and 5 images (electrogrammes) are entered into the program "GDV Capture".

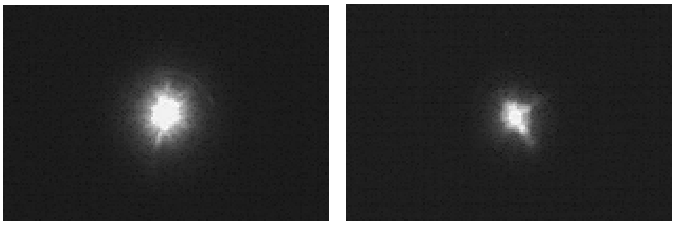
GDV electrogramms were captured with gas discharge visualization camera "GDV Camera Pro" with accessories from the "GDV Mini-Lab" for liquid analysis. The data was recorded in a computer programme "GDV Capture" and processed in "GDV Scientific Laboratory". The resulting parametric analysis was made by "Microsoft Excel" software.

The programme "GDV Scientific Laboratory" calculates 12 parameters for each electrogramme. Major characteristics of the radiation are area, intensity, form coefficient and entropy. Area and intensity characterize the object's energy potential. GDV electrogrammes area assessed by the number of pixels in image, but the intensity is the pixel brightness. Form coefficient characterizes size of the edge indentations of the image (the larger form coefficient, the higher score), but entropy is the measure of informativity and deviations from equilibrium - it decreases, approaching equilibrium.

In testing methodology methods of mathematical statistics are used to reduce variation of key parameters and to indicate dependent variables, which are sensitive to metal ions in the liquid.

IV. RESULTS

Electrogrammes of contaminated (Fig. a) and unpolluted (Fig. b) water show increase of area after addition of zinc oxide nanoparticles in distilled water.



a b

Fig. 2. Distilled water electrogramms: a - with zinc nanoparticles polluted water, b - non-contaminated water.

3 shows the graph of comparative average area values for all objects of the experiment - contaminated (1 Zn, 2 Zn and 3 Zn) and unpolluted water (control), calculated from electrogrammes with fixed intervals 3, 5 and 7 seconds. It is seen from graphs of Fig. 3 that time intervals between electrogrammes fixation have not significant influence on their average area values, while differences between variants with the different quantities of zinc oxide nanoparticles in solution and pure distilled water are significant for all three samples - 3 Zn sample area increase compared to the control water in average by 79%, 2 Zn sample - 143%, and 1 Zn sample - 174%.

Taking into account that 1 Zn water sample was added the highest dose of zinc oxide nanoparticles, but the 2 Zn lower and 3 Zn smallest amount of nanoparticles, conclusion could be formulated: 1) average areas of electrograms could reflect the presence of zinc oxide nanoparticles in distilled water; 2) different nanoparticles concentrations has significant affect on area values of electrogrammes. Thereby in further studies the area mean value is considered as perceiving parameter if the sample prepared for testing has been washed in distilled water.

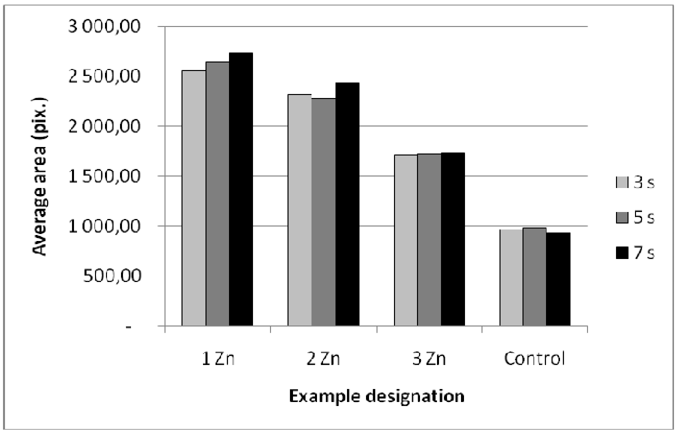


Fig. 3. Mean values of area for water polluted with zinc nanoparticles and unpolluted water.

Figure 4 shows the average intensity results for contaminated and uncontaminated water, showing a comparatively smaller difference between pure water and with zinc oxide nanoparticles-contaminated water (3 Zn - 10%, 2 Zn - 13%, 1 Zn - 14%). As in the previous figure, the graph shows that the time intervals between electrogrammes fixed moments have no constitutive impact on results.

Intensity, unlike the area did not show such a pronounced difference between the various gradations of zinc oxide nanoparticles volume in samples (1 Zn, 2 Zn and 3 Zn), the difference is only 1-3%.

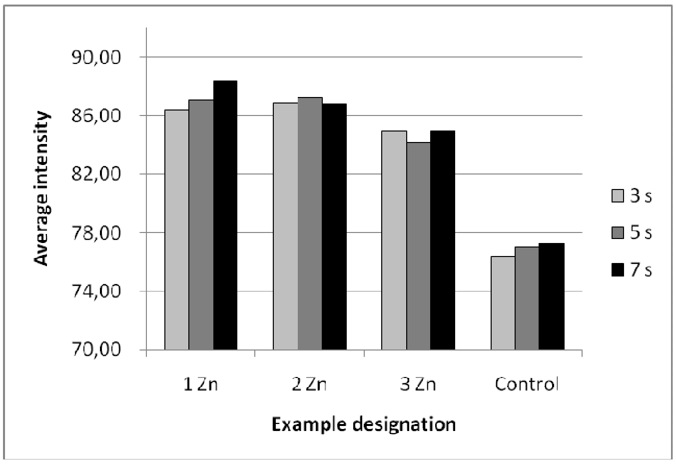


Fig. 4. Mean values of intensity for water polluted with zinc nanoparticles and

Figure 5 shows the average form coefficient parameters for all experimental subjects. In contrast to the area and intensity parameters, the form coefficient shows no significant differences between polluted and unpolluted water. Only the samples with the highest degree of contamination (1 Zn) produce a small form factor growth - by 4.5%.

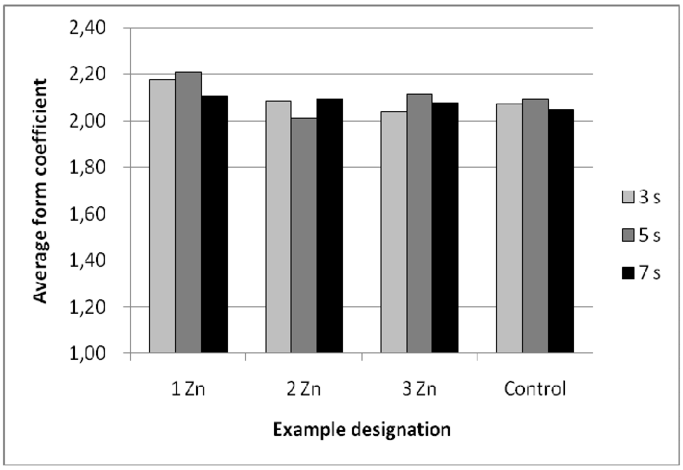


Fig. 5. Mean values of form coefficient for water polluted with zinc nanoparticles and unpolluted water.

The average entropy values (Figure 6) at the lowest concentration (3 Zn) decreases, similar results are also for the medium variant (2 Zn), while at higher concentrations slightly increased (1 Zn). In total contaminated water entropy changes compared with distilled water are relatively small – for 1 Zn sample it has increased by 0.6%; 2 Zn sample - decreased by 6.1%; 3 Zn sample - decreased by 5.2%.

Analyzing the results of the experiment, for each data package the average relative standard error has been calculated. For contaminated water measurements the average relative standard error is less than 2.75% limit, but for uncontaminated water, it reaches 2.79%, so that all data units have sufficient reliability.

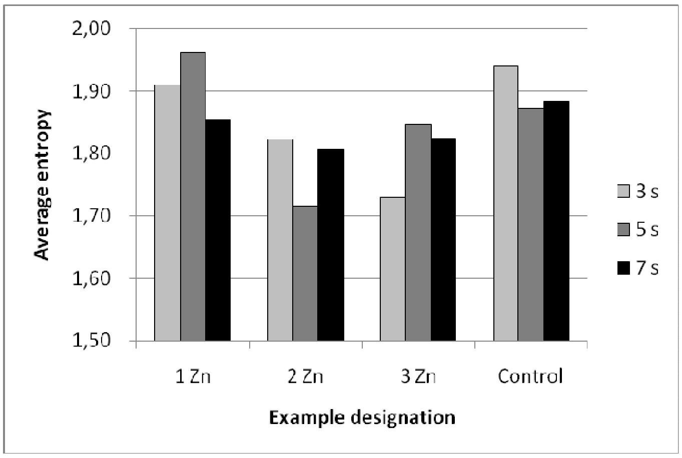


Fig. 6. Mean values of entropy for water polluted with zinc nanoparticles and unpolluted water..

Area range between highest and lowest values (Fig. 7.) is the highest for contaminated water, and it is growing, increasing the concentration of zinc oxide nanoparticles. Such a result is acceptable, being aware that with the increase of the area of electrogramme, there is also a greater mutability.

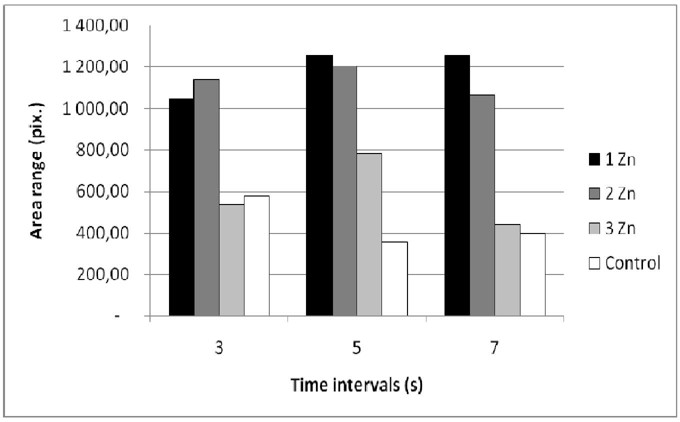


Fig. 7. Area range for water polluted with zinc nanoparticles and unpolluted water

Comparing the results obtained in this experiment with data from an equivalent experiment, which analyzes the impact of copper nanoparticles on water parameters, washing in distilled water with copper nanoparticles coated fabric [5], it appears that in both cases the most sensitive are area parameters on the nanoparticles pollution in water. After washing the textile detached copper nanoparticles resulted increase of the area by an average of 43%, compared with uncontaminated distilled water (Fig. 8).

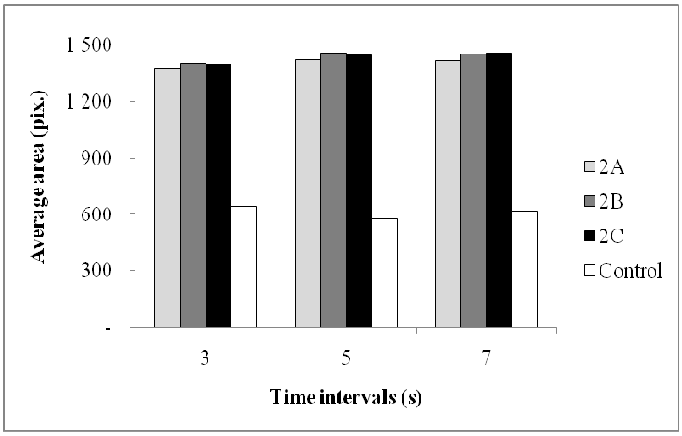


Fig. 8. Mean values of area for water with copper nanoparticles and unpolluted water [5].

In experiment with copper nanoparticles coated fabrics a greater sensitivity to metal ions presence in water showed the entropy parameters - 44% compared with uncontaminated water (Fig. 9). By contrast, zinc nanoparticles did not lead to persistent changes in the entropy indicators (Fig. 6).

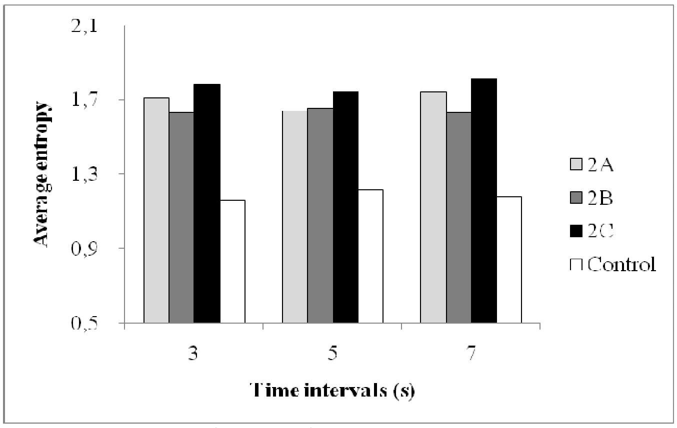


Fig. 9. Mean values of entropy for water with copper nanoparticles and unpolluted water [5].

In parameters of intensities in both cases the differences are smaller than the indicators of area, however, in experiment with a copper nanoparticles increase is higher - 14% (Fig. 10), but in experiment with zinc oxide nanoparticles only 1-3% (Fig. 4).

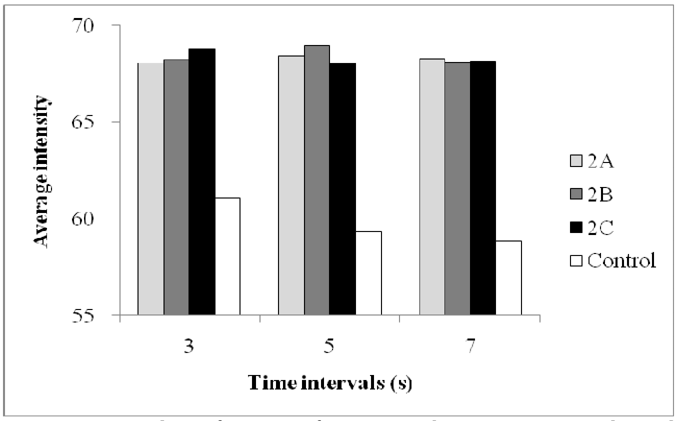


Fig. 10. Mean values of intensity for water with copper nanoparticles and unpolluted water [5].

Form coefficient parameters copper ions showed the least - an increase compared with the control water was only about 7% [5]. While the effects of zinc oxide nanoparticles in distilled water showed only form coefficient for sample with the highest degree of contamination - and they are only 4.5% (Fig.5).

V. CONCLUSIONS

The results confirm the suitability of GDV equipment for textile zinc oxide coating resistance testing. The differences between polluted and unpolluted water can be evaluated visually by looking at the acquired electrogrammes.

Testing of distilled water with and without zinc oxide nanoparticles, showed a significant difference between polluted and unpolluted water within concentration intervals 0.5 to 1.5%, as average area values of contaminated water electrogrammes are more than 2.5 times higher than unpolluted distilled water area. In addition, area values as indicators can recognize sample pollution intensity. At the same time form coefficients did not show significant differences between polluted and unpolluted water, it may be more pronounced difference appears at higher pollution concentrations. As entropy indicators in this experiment show results under discussion, they could not usable for detection of zinc oxide nanoparticles concentration in water.

Compared to the experiment discussed in this article, which analyzes the impact of zinc oxide nanoparticles on distilled water, and the previously published article, which analyzes the effects of copper nanoparticles on distilled water, it is concluded that the presence of zinc oxide nanoparticles cause a greater change in the electrogram areas, while remaining GDV parameters did not show such large changes, as in experiment with copper ions. It is hypothetically possible that the area most accurately shows the pollution levels, however, to prove it, it is necessary to carry out additional experiments.

The data presented in the article are interim results, in the further developments of method it is necessary to monitor water radiation changes, by adding to a water even smaller amount of zinc oxide nanoparticles in order to determine the critical threshold at which the differences between polluted and unpolluted water in the electrogrammes are no longer fixed. In addition, in experiments it is required to use other metal nanoparticles, to make comparative studies. Thus it is possible to elaborate economic and high-speed testing method, which does not require prior sample preparation. GDV method can be used by product designers, manufacturers and users to verify the persistence of textile metal coating, thereby creating environmentally friendly textiles with high added value.

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Eva Trumsiņa, Silvija Kukle, Gunta Zommere. Cinka nanodaļiņu ietekme uz destilēta ūdens parametriem
Rakstā apskatīti jautājumi, kas saistīti ar tekstilmateriālu metāla nanodaļiņu pārklājumu noturību mazgāšanas laikā, sevišķu uzmanību veltot pētījumiem par iespējām konstatēt cinka nanodaļiņu klātbūtni un koncentrāciju notekūdeņos. Pētījumā izmantota gāzizlādes vizualizācijas iekārta (GDV kamera) un papildaprīkojums šķidrumu analīzei.
Dažādu metālu nanodaļiņu lietojuma spektrs pēdējos gados ir strauji pieaudzis, t.sk. apģērbā un mājturības precēs. Galvenie riski, kas saistīti ar metālpārklātu tekstilmateriālu lietošanu, ir metāla nanodaļiņu atdalīšanās no materiāla lietošanas un kopšanas laikā.
Zināmās metodes, kas tiek izmantotas nanodaļiņu testēšanai ūdenī, ir mikroskopijas metodes, lietojot tādus mikroskopu tipus kā transmisijas elektronu mikroskops, skenējošais elektronu mikroskops un atomspēku mikroskops. Nanodaļiņu analīzei bieži tiek izmantotas arī uz Brauna kustības aprēķiniem balstītas iekārtas - Fotonu korelācijas spektroskopija un Nanodaļiņu trases analizators.
Lai pārliecinātos, ka elektrogrammu parametros atspoguļojas metāla nanolīmeņa daļiņu/jonu klātbūtne ūdenī, destilēts ūdens apzināti tika piesārņots ar cinka nanodaļiņām. Salīdzināšanai izmantots nepiesārņots destilēts ūdens. Eksperimenta rezultāti apliecina GDV iekārtas piemērotību tekstilmateriālu cinka pārklājumu noturības testēšanai. Testējot destilētu ūdeni ar un bez cinka nanodaļiņām, konstatēta būtiska atšķirība starp piesārņotu un nepiesārņotu destilētu ūdeni, to apliecina iegūto elektrogrammu laukuma rādītāji – ar cinka nanodaļiņām piesārņota ūdens elektrogrammu laukums ir pat vairāk nekā 2.5 reizes lielāks nekā nepiesārņota destilēta ūdens laukums. Turklāt laukuma rādītājos uzskatāmi nolasāma ūdens paraugu atšķirīgā piesārņojuma intensitāte, kas izpaužas kā atšķirības starp piesārņoto ūdens paraugu elektrogrammu laukuma dimensijām pikseļos.
Veicot papildus pētījumus, iespējams iegūt ekonomisku un ātrdarbīgu testēšanas metodi, kurai nav nepieciešama iepriekšēja paraugu sagatavošana.

Эва Трумсиня, Сильвия Кукле. Влияние цинковых наночастиц на параметры дистиллированной воды
В статье рассматриваются вопросы, связанные со стабильностью покрытия металлических наночастиц текстиля во время умывания, обращая особое внимание на исследования по возможности выявить присутствие и концентрацию цинковых наночастиц в сточных вод. В исследовании было использовано устройство газоразрядной визуализации (ГРВ камера) и аксессуары для анализа жидкостей.
Диапазон приложений различных металлических наночастиц в последние годы резко возросло, в том числе в одежде и товаров для дома. Основные риски, связанные с использованием металопокритого текстиля, отделение металлических наночастицы от материала во время использования и ухода.
Известные способы использующиеся для тестирования наночастиц в воде, основаны на микроскопии, используя такие типы микроскопов, как просвечивающий электронный микроскоп, сканирующий электронный микроскоп и атомно-силовой микроскоп. В анализе наночастиц часто используется оборудование, основанное на расчете движения Брауна - спектроскопия корреляции фотонов и анализатор трассировок наночастиц.
Чтобы убедиться, что в параметрах электрограммов отражено присутствие металлических частиц / ионов в воде, намеренно была загрязнена дистиллированная вода с наночастицами цинка. Для сравнения использовалась незагрязненная дистиллированная вода. Результаты подтверждают пригодность оборудования ГРВ в тестирование устойчивости цинковых покрытиях текстиля. Тестирование дистиллированной воды с и без наночастиц цинка показало существенное различие между загрязненной и незагрязненной дистиллированной водой, это доказывает показатель и площади электрограмм - площадь электрограмм, воды загрязненной наночастицами цинка, более чем в 2,5 раза выше, чем у незагрязненной дистиллированной воды. Кроме того, показатели площади наглядно демонстрирует различную интенсивность загрязнения образцов воды, в которых выдны различия между размерами площади электрограммов в пикселях загрязненных проб воды.
При проведении дополнительных исследований в результате можно получить экономический и высокоскоростный метод тестирования, который не требует предварительной подготовки образца.