

Laser technologies for detection nanoparticles in environmental media

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Nanoparticles detection and concentration gradient of trace elements in natural waters after nanoparticles destruction and without it are main aims of this paper. Nanoparticles were detected in spring waters using dynamic light scattering and measured about 200 nm in the samples of Essentuki No17 and 10 nm in the samples of Novoterskaya and Narzan. Determining the concentration of Ni, Cr and Mn after mineralization in hard conditions (microwave mineralization) showed increasing concentration of trace elements in 10 times. Destruction of nanoparticles and elements release cause this increasing of concentration.

1. Introduction

The surface microlayer (biofilm) enriched by hazardous compounds up to 100-10000 times higher concentration than bulk water is main source of the marine aerosols. Accumulation of the hazardous compounds in marine biofilm occurs as natural adsorption from bulk water. A natural wind-wave interaction between atmosphere and ocean is most important in generation of toxic marine aerosols. Carrying and mixing of marine aerosols with terrestrial ones and additional concentration of hazardous substances due to evaporation of water from aerosol particles. A stream of the polluted aerosols has a negative influence on coastal ecosystems and human health, a monitoring of marine aerosols plays an important role in state of environment in coastal regions.

Processes of mineral destruction and aerosol generation, chemical and biological processes, industrial pollution are most important in formation of nanoparticles in natural waters. There are four chemical groups of natural nanoparticles: aluminosilicates and silicates, biogenic, inorganic and carbonic nanoparticles. Most of trace elements in natural waters are occluded or adsorbated on nanoparticles (including aluminosilicates) that play an important role in trace elements delivery, that's why monitoring of nanoparticles plays an important role in analysis of mineral waters.

1.1 Origin and composition of nanoparticles in natural water

Principal mechanisms of natural water and near-water air stratum nanoparticles producing include dispersion of minerals by interaction with atmosphere and water; aerosols producing from water surface by wind-wave interaction and other mechanical or chemical effects (Goncharuk et al., 2005); biogenic formation related to metabolic

discharge, especially bacterial, protozoan, algae sub-cell structures, and dying off metazoan tissues (Wigginton et al., 2007); chemical producing based on colloids formation and oxidizing interactions, e.g. marine aerosols formation by atmospheric air ionization (Lapshin et al., 2007); anthropogenic mechanism closely related to atmospheric and water pollution by carbonic particles (Mueller et al., 2008, Zhu et al., 2006). The most powerful sources of nanoparticles are water surface of seas and oceans (wind-wave interaction) and the minerals “washing-out” by ground and surface waters.

1.2 Chemical groups of natural nanoparticles

According to basic mechanisms of nanoparticle formation four chemical groups of natural nanoparticles can be noted:

Aluminosilicates and silicates

These nanoparticles generally include d-elements. Occluded in nanoparticles heavy metals analyzing after acidic sample preparation are quantitative indicators of aluminosilicates presence (Holm and Roberts, 2007).

Biogenic nanoparticles

Differences of biopolymers explain a variety of these particles. There are prevalent polypeptide and nucleoprotein particles produced in biogeochemical active areas, e.g. plankton, benthon, communities of birds and mammals etc (Dufresne, 2006), also lignic and humic particles (De Momi and Lead, 2008).

Inorganic nanoparticles

Generally consist of heavy metals oxides, e.g. ferric, lead, copper etc (Weisner, 2008).

Carbonic particles

Anthropogenic and biogenic nanoparticles.

It should be noted a combination of above mentioned groups of nanoparticles. Occluded or adsorbed compounds occurred fairly often could change prevailing component in chemical compositions.

1.3 Geochemical characteristics of mineral waters

Mineral ground waters formed in the earth stratum with geothermic, hydrologic and geochemical peculiarities are characterized by localization, gas, saline and trace elements composition. Mineral waters classification is based on the prevalence of most important characteristics. Varieties of geochemical processes are of primary importance in ground water chemical composition formation.

Formation of carbon dioxide waters related to deep buried neointrusive hotbeds activity. Allowing to superstratum along the deep breaks carbon dioxide carries a lot of specified elements: boron, arsenic, silicates, fluorine, lithium, iron etc. Gypsum and prevalent sulfide minerals dissolution and its oxidizing allow to sulfate calcic and sodium waters appearance. Chloride sodium and calcic waters form in measure of aquifers occurrence and are prevalent in underground hydrosphere. Processes of sulfide minerals oxidizing and organic substances desulfatization allow to sulfide waters formation. Formation of iodine and bromine waters is a result of their redistribution in “rock-water-organic substances” system for diagenesis. Silicon in ground waters offers methasilicic and orthosilicic acids and its salts as colloids. Trace elements enriched waters, e.g. ferruginous arsenic waters are located in most carbon dioxide sources. Its genesis is unknown.

2. Materials and methods

For analysis three trademarks of mineral water was chosen: Novoterskaya Tselebnaya, Narzan and Essentuki No17 (Russia). Nanoparticles in three samples of each trademark were detected by dynamic light scattering (DLS) using Zetasizer Nano ZS (Malvern Instruments). For measuring the concentration of occluded trace elements the graphite Zeeman AAS was applied. Concentration of Ni, Mn and Cr was measured with atomic-absorption spectrometer "Spectr AA-800" (Varian); microwave oven MDS2000 for mineralization was applied. Current of emitters "Spectr AA": for Ni, Cu, Hg, Cd – 4.0 mA; Al, As – 10 mA; Mn, Zn – 5.0 mA; Cr, V, Pb – 7.0 mA, Co, Sn – 7.0 mA. Monochromator slot for Al, Ni, Cu, Zn, Hg – 0.5 nm; Cr, Fe, Mn, V, Co, Sn – 0.2 nm, Cd, Pb, As – 1.0 nm. Wavelengths and modifiers: Al - 256.8 nm, Mg(NO₃)₂; Ni - 232.0 nm, Mg(NO₃)₂; Cr - 429.0 nm, Mg(NO₃)₂; Mn - 403.1 nm, Mg(NO₃)₂; Fe - 386.0 nm, Mg(NO₃)₂; Cu - 327.4 nm, Pd(NO₃)₂; Zn - 307.6 nm, Mg(NO₃)₂, As - 193.7 nm, Pd(NO₃)₂+Mg(NO₃)₂; Sn - 286.3 nm, Mg(NO₃)₂ + NH₄H₂PO₄; V - 318.5 nm; Co - 242.5 nm, Pd(NO₃)₂; Cd - 228.8 nm, Pd(NO₃)₂+Mg(NO₃)₂+NH₄H₂PO₄; Pb - 283.3 nm, Pd(NO₃)₂+Mg(NO₃)₂+NH₄H₂PO₄. Specific standard deviation was not more than 20% for confidence probability 0.95. The reference material fit with Reference Sheet IAEA-405 (2000).

Following sample preparations were used:

- 1) interaction with aqua regis: to 1 ml of water add 0.5 ml of aqua regis;
- 2) interaction with aqua regis and microwave mineralization: to 1 ml of water add 0.5 ml of aqua regis and mineralize in microwave oven during 2 min at 80% capacity and 5 min at 100% capacity;
- 3) interaction with aqua regis and hydrofluoric acid and microwave mineralization: to 1 ml of water add 6 ml of mix HCl+HNO₃+HF and keeping during 1 day. Then mineralize in microwave oven during 2 min at 80% capacity and 5 min at 100% capacity.

Each sample of mineral water was degased before measuring with heating and further cooling at the initial temperature.

3. Results and discussion

The graphite Zeeman atomic-absorption spectrophotometry is optimum method for monitoring of the mineral waters elemental composition over the high specificity and selectivity and low threshold of detectability. Analyze of Ni, Cr, and Mn allowed finding the depending on the sample preparation considerable concentration spread of these elements (table 1).

Table 1 Concentration spread of Ni, Mn, and Cr in Narzan sample (n=6) (mg/l)

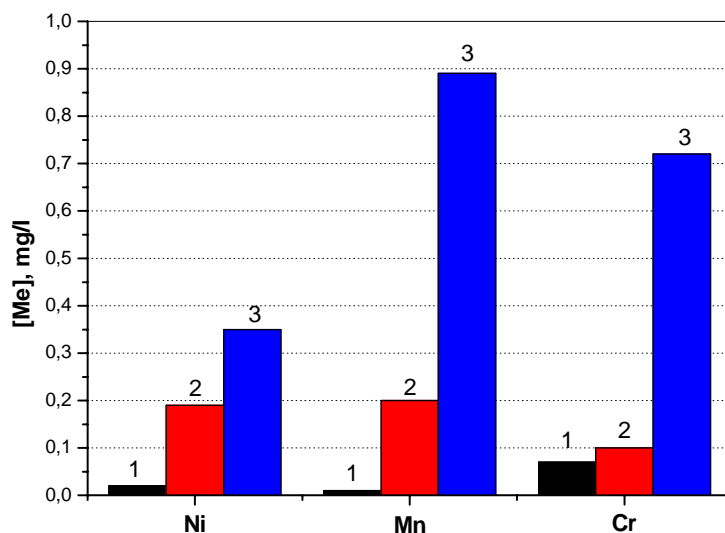
Ni			Mn			Cr		
1	2	3	1	2	3	1	2	3
0.02	0.19	0.35	0.01	0.20	0.89	0.07	0.10	0.72

1 - interaction with aqua regis;

2 - interaction with aqua regis and microwave mineralization;

3 - interaction with aqua regis and hydrofluoric acid and microwave mineralization.

Figure 1 Trace elements concentration spread in sample Narzan



Concentration of copper was constant regardless of sample preparation and had values 0.23-0.33 mg/l. Concentration gradient of V, As, Cd, and Pb was slight and in standard error range because of low modulus of concentration. Our results follow that sample preparation in hard conditions (mineral acid and microwave mineralization) is necessary for most full trace elements concentration measuring in samples. Nanoparticles in the samples of mineral waters were detected by dynamic light scattering with Zetasizer Nano ZS and their values are about 200 nm in Essentuki No17 and 10 nm in Novotorskaya Tselebnaya and Narzan. This method is most good because the measurement range is from 0.4 nm to 6 μ m and background is not required.

The results of heavy metals concentration measuring and dynamic light scattering show the trace elements are really occluded on detected in natural waters dispersive phase. It is evidence of the nanoparticles in mineral waters play an important role in trace elements delivery, monitoring of nanoparticles is important for analysis of mineral waters. Discovered in mineral waters high concentration of Al corroborate the aluminosilicic nature of ground mineral water dispersive phase.

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