PREPARATION AND CHARACTERIZATION OF LOW CONCENTRATED SUSPENSIONS OF INDUSTRIAL NANOPARTICLES

Karepina Elizaveta[1,2], Hadioui Madjid[2], Godymchuk Anna[2,3]

Supervisor: prof. Wilkinson Kevin James[2]

[1] National University Tomsk Polytechnic University, Russia, Tomsk, Lenina ave., 30, 634050

[2]University of Montreal, 2900 Boulevard Edouard-Montpetit, Montréal, QC H3T 1J4

[3]National University of Science and Technology "MISIS", Leninsky ave., 4, Moscow, 119991, Russia

E-mail: karepina_ee@mail.ru

ПОДГОТОВКА И ИЗУЧЕНИЕ РАЗБАВЛЕННЫХ СУСПЕНЗИЙ ПРОМЫШЛЕННЫХ НАНОЧАСТИЦ

Карепина Елизавета, Хадиуи Маджид, Годымчук Анна

Научный руководитель: профессор Уилкинсон Кевин Джеймс

[1] Национальный исследовательский Томский политехнический университет,

Россия, г.Томск, пр. Ленина, 30, 634050

E-mail: karepina_ee@mail.ru

[2]Монреальский университет

2900 Бульвар Эдуарда Монпети, Монреаль, Квебек, H3T 1J4

[3]Национальный исследовательский технологический университет «МИСИС»

Ленинский проспект, 4, Москва, 119991, Россия

В настоящее время одним из наиболее первпективных и развивающихся методов исследования размеров наночастиц является масс-спектрометрия с индуктивно связанной плазмой по методу единичных частиц (SP ICP-MS), позволяющая исседовать частицы в очень низких эколонически-эквивалентных концентарциях. В настоящей работе рассмотрены различные метдики приготовления суспензий промышленных наночастиц для исследования с помощью SP ICP-MS, выбраны оптимальные условия и представлены первые результаты.

The release of metal (and/or metal oxide) nanoparticles, such as Ag, Cu, Ni, Zn, TiO2 and ZnO, into the environment and, hence, their inevitable interactions with natural biota are a direct consequence of the drastic increase in the production and applications of industrial nanopowders [1]. Unfortunately, due to the lack of data on the physicochemical properties of industrial nanomaterials, it is difficult to predict their impacts on the environment. Therefore, it is of great interest to develop methods and approaches that would allow us to better characterize and track the fate and the behavior of metal nanoparticles in the environment, especially in aqueous media.

Single Particle Inductively Coupled Plasma Mass Spectrometry (SP ICP-MS) is the most (if not the only one) appropriate technique for environmental aqueous media where the concentration of metal nanoparticles is expected to be very low. In addition to the capability of measuring environmentally relevant concentrations (i.e. ng/L), SP ICP-MS allows also simultaneous determinations of both dissolved and particulate metal, as well as particle size distribution and particle number concentration [2-5]. SP ICP-MS requires highly diluted suspensions of nanoparticles suspensions (typically below 2 µg/L). However, due to inaccuracy in weighting

very small amounts of powder, consecutive dilutions of a stock suspension of nanoparticles until reaching the required concentration would be the most acceptable approach leading to homogeneous suspensions of industrial nanopowders. The main purpose of this study was the optimization of the procedure of suspending industrial nanoparticles in aqueous medium and their analysis by SP ICP-MS. Industrial nanoparticles of Cu, Ni, and Zn (average diameter of 100 nm, produced by "Advanced Powder Technology", Tomsk, Russia) were studied. The stock suspension of nanopowders was prepared by adding 50 mg of dry nanopowder to 50 mL of 10^{-2} M HEPES buffer solution, pH 5-7 (powder concentration of 1 g/L). The suspension was then diluted to 100 ng/L using different stirring methods: hydrodynamic, sonication and magnetic. The concentrations of the suspensions were determined by a PerkinElmer NexION 300X Inductively Coupled Plasma Mass Spectrometer (ICP-MS, University of Montreal).

It was found that obtaining the predetermined concentration by dilution in buffer solution was unlikely to be effective in the case of industrial nanoparticles due to the high tendency to aggregation and low stability in aqueous medium. Large aggregates, prone to sedimentation, were immediately formed in the freshly prepared suspension. Non-aggregative portion of sample remained in the supernatant forming a suspension of small flake-oxide-hydroxide composition. The standard deviation of 5 measurements using any method of dispersion exceeded 600%.

To avoid aggregation of nanoparticles different stabilizers, including the carboxylate anions [6], amino acids and fulvic acids [7] are generally used. In this study the fulvic acid was used as a natural organic matter. Suspensions were prepared as described above using a solution of 100 mg/L of fulvic acid for dilution. The obtained results showed that fulvic acid doesn't provoke disaggregation of agglomerates. The standard deviation was about 500%. Thus, fulvic acid was not effective in stabilizing suspensions of Cu, Ni and Zn within pH 5-7.

According to the obtained results, suspensions were prepared by separation: highly concentrated suspensions were prepared by adding 100 mg of dry nanopowder to 50 mL of Milli-Q water, corresponding to a concentration of 2 g/L. The resulting suspensions were placed in an ultrasonic bath (Branson V5510, 20 °C, 40 kHz, 60 min). Then, the suspensions were stirred hydrodynamically (Fisher Scientific ™ Digital Vortex Mixer) at 3000 rpm for 1 min and centrifuged for 30 min at 4000 rpm. After centrifugation the supernatant was immediately diluted 10 times with Milli-Q water for SP ICP-MS analysis and 10 times with 1% (v/v) HNO_3 for total metal quantification. Following this procedure, the resulting concentration was found reproducible (Figure 1). Furthermore, the experiment showed that using the remaining sample precipitate instead of dry powder following the same procedure (suspension in Milli-Q water, ultrasonics and hydrodynamic stirring, centrifugation, successive dilutions of supernatant with MilliQ and HNO_3 and analysis) led to quite similar results of metal concentration in the supernatant as shown in Figure 2 for triplicate extractions.

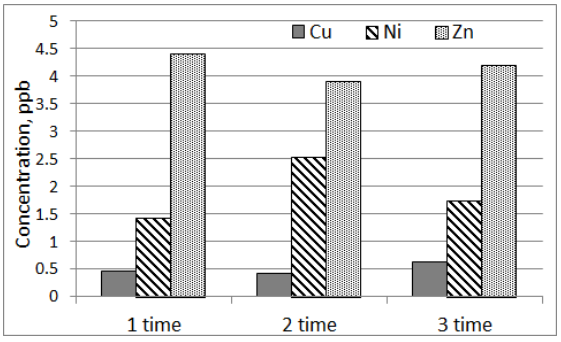

Fig. 1. The reproducibility of the resulting stock-suspension concentration

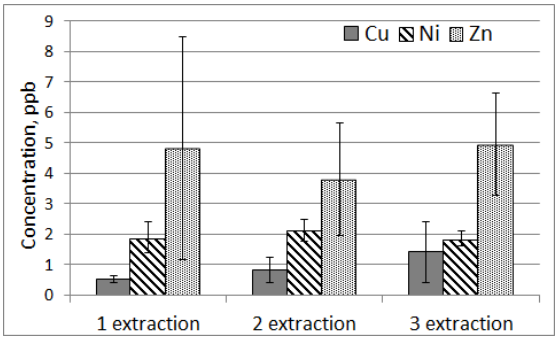

Fig. 2. Stock suspension concentration during the three extractions from one sample

The example of particle size distribution produced with SP ICP-MS coupled ion exchange resin, is shown in Figure 3. According this result, studied powder is very polydisperse, particles size varies from 40 till 480 nm.

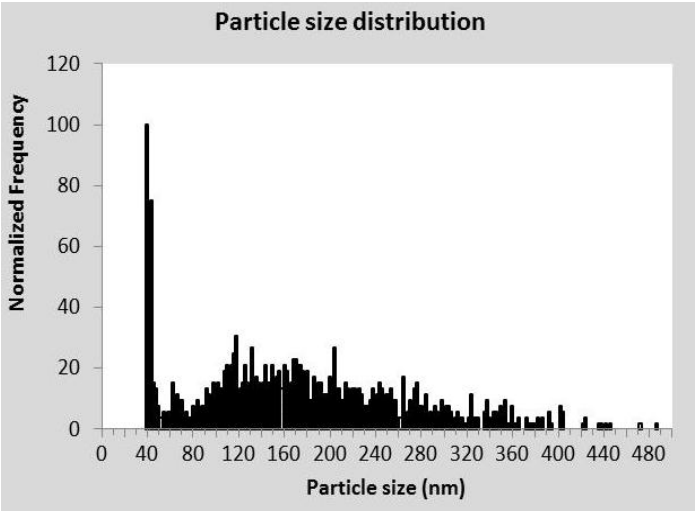

Fig. 3. Particle size distribution of Ni nanopowder

The work was supported with the Russian Fund for Fundamental Research (project # 15-03-06528).

REFERENCES

1. Marques M.R. C., Loebenberg R., Almukainzi M. Simulated biological fluids with possible application in dissolution testing // Dissolution Technologies. – 2011 – Vol. 118. – P. 15-28.

2. Perdue E.M. Standard and reference samples of humic acids, fulvic acids, and natural organic matter from the Suwannee River, Georgia: thirty years of isolation and characterization // In Xu, J.; Wu, J.; He, Y. Functions of natural organic matter in changing environment -. Springer Netherlands: 2013. – pp 85-88.

3. Hadioui M., Peyrot C., Wilkinson K.J. Improvements to single particle ICPMS by the online coupling of ion exchange resins // Analytical Chemistry – 2014 – Vol. 86. – P. 4668-4674.

4. Laborda F., E. Bolea and J. Jimenez-Lamana. Single particle inductively coupled plasma mass spectrometry: a powerful tool for nanoanalysis // Analytical Chemistry. – 2014. – Vol. 86. – P. 2270-2278.

5. Mitrano D. M., Barber A., Bednar A., Westerhoff P., Higgins C.P., Ranville J.F. Silver nanoparticle characterization using single particle ICP-MS (SP-ICP-MS) and asymmetrical flow field flow fractionation ICP-MS (AF4-ICP-MS) // Journal of Analytical Atomic Spectrometry. – 2012. – Vol. 27. – P.1131-1142.

6. Sharifi S., Behzadi S., Laurent S., Forrest M.L., Stroeve P., MahmoudiM. Toxicity of nanomaterials // Chemical Society Reviews. – 2012. – Vol. 41(6). – P. 2323-2343.

7. Tuoriniemi J., Cornelis G., HassellovM. . Size discrimination and detection capabilities of single-particle ICPMS for environmental analysis of silver nanoparticles // Analytical Chemistry. – 2012. – Vol. 84(9). – P.3965-3972.