Determination of Size and Concentration of Nanoparticles in Seawater With the icpTOF Quantistar

Olga Borovinskaya[1], Lyndsey Hendriks[1],
Mohammed Baalousha[2]
1-TOFWERK, Thun, Switzerland
2-University of South Carolina, USA

Introduction

Single particle inductively coupled plasma mass spectrometry (sp-ICP-MS) has been readily applied to characterize nanoparticles in complex samples [1] such as animal tissues [2], whole blood [3], chicken meat [4], and sanitary sewage spills [5].

A widely used calibration method proposed by Pace et al. [6] for sp-ICP-MS generates accurate results only if nanoparticles and standard materials are dispersed/dissolved in the same media. Therefore, in most studies, complex matrices are digested, and samples are consequently diluted in ultrahigh purity (UHP) water. Alternatively, particles can also first be extracted and then re-suspended in UHP water prior to sp-ICP-MS measurements. Sample preparation is time consuming and can potentially alter the particle characteristics. Element standards must also be prepared in the same matrix as samples which can compromise their stability. Additionally, although widely applied, this calibration approach requires standard nanoparticle reference materials which are not always readily available.

The Quantistar in combination with the icpTOF offers an alternative online calibration approach using microdroplets as calibrants. A sample containing nanoparticles is introduced via a nebulizer/spray chamber and the droplets of element standards are added inline to the sample aerosol [7]. This method does not require matrix matching between the sample and the standard, because the calibrant droplets are injected into the ICP at the same time as the sample and experience the same plasma conditions. Consequently, thanks to

the simultaneous introduction all nebulization- and plasma-related matrix effects are accounted for, and accurate particle mass and particle number concentration (PNC) are obtained with no or little sample preparation.

Application Example: Quantification of Pt Nanoparticles in Seawater

Monodisperse Pt citrate capped nanoparticles of 70 nm nominal size were synthesized and characterized by Sikde et al. [8]. In this study, the particles were dispersed in 1) UHP water, 2) a 1:5 mixture of seawater and UHP water, and 3) a 1:10 mixture of seawater and UHP water. Particle size and PNC were measured in these three matrices using the icpTOF with both the conventional calibration method by Pace et al. and the microdroplet online calibration method. For the Pace calibration method, Pt element standards, Au element standards, and Au 50 nm particles (NanoComposix) were prepared in UHP water. The size-based approach was used for determination of the sample transport efficiency [6]. For the online microdroplet calibration method, Pt standards were prepared in 1% nitric acid as a most stable medium and the same analysis workflow as described by Hendriks et al. [9] was applied. PNC was quantified by adding Cs tracer of a known concentration to both samples and standards using the method reported by Mehrabi et al. [10].

The size determined using the Pace method in UHP water was of 76±6 nm (size standard deviation of 1500 particles) and is very close to the size of 77±1 nm (size standard deviation of 3 replicates) determined by Sikder et al.[8] using the same method. For Pt NPs spiked with seawater, matrix effects are expected. Indeed, sodium salt in seawater suppresses the Pt signal proportionally to its concentration. In fact, this suppression was so strong in pure seawater that no Pt particles could be detected. Consequently, using the conventional calibration approach, which cannot compensate for matrix effects, i.e for the signal suppression, the calculated sizes of Pt NPs decreased from 76±6 nm down to 41±6 nm with increasing seawater content (Figure 1). The decrease in calculated particle number concentration was ca. 30% and is most likely due to different nebulization efficiencies of diluted seawater and UHP water and, to a smaller extent, due to aggregation of particles in salty matrix.

The size of 71 nm±5 nm determined in UHP water by online microdroplet calibration was closer to the sizes measured by AFM (71 nm), by TEM (73 nm), and by DLS of 71 nm [8]. The determined size was independent of the sample matrix and the change in particle number concentration was <8% (Figure 2). A minor decrease in

the number of detected particles as well as broadening of the size distribution histogram with the icpTOF Quantistar (size RSD of 7%, 10%, and 13% for milliQ, 1:10 seawater:milliQ, and 1:5 seawater:milliQ, respectively) can partially be attributed to particle aggregation induced by sodium salt matrix as also reported by Sikder et al. [8]. The signal intensity per particle decreases with increasing the seawater content which causes the observed RSDs to increase as well. The same size distribution histogram broadening was also observed in the standard calibration method (size RSD of 8%, 11%, and 14% for milliQ, 1:10 seawater:milliQ, and 1:5 seawater:milliQ, respectively).

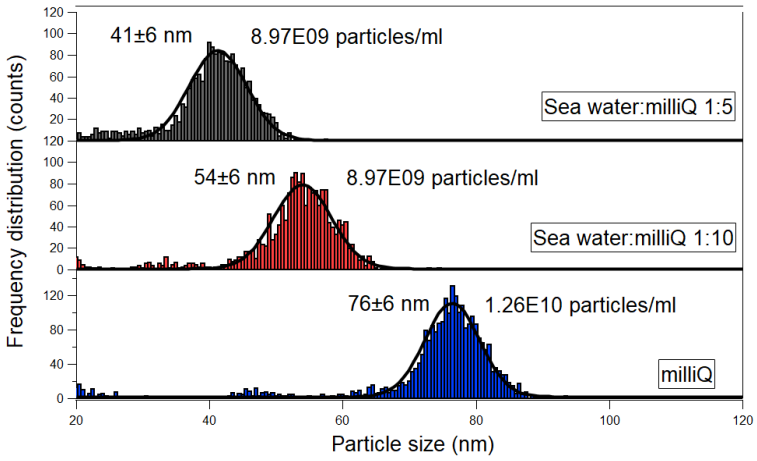

Figure 1. *Size and particle number concentration of Pt nanoparticles determined using Pace calibration method.*

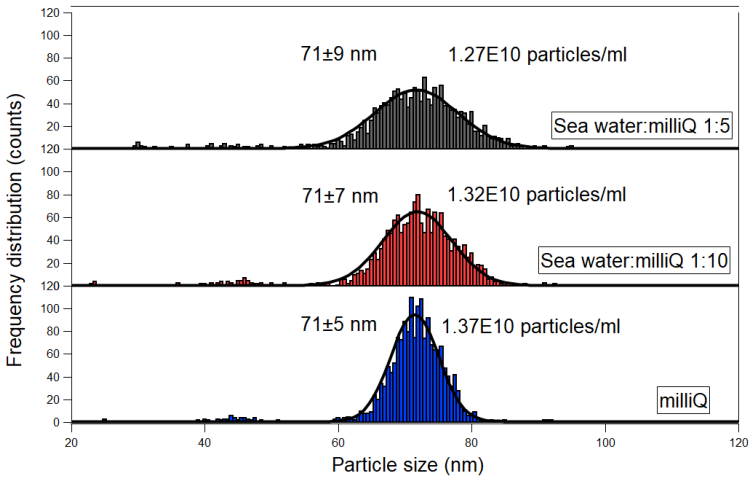

Figure 2. *Size and particle number concentration of Pt nanoparticles determined by using the combination of the Quantistar and the icpTOF with the online microdroplet calibration method.*

Conclusion

The standard calibration method for sp-ICP-MS works well in simple matrices such as UHP water but fails to generate accurate results for particles dispersed in more complex matrices such as seawater. By using the icpTOF in combination with the Quantistar, both particle size and particle number concentration can be accurately determined in various complex matrices as shown in this application example with Pt particles in seawater. The online microdroplet-based calibration method is simple, fast, and robust and can be applied for the characterization of a range of samples, such as soil suspensions, particles in biological matrices, or for single cell analysis in biological buffers.

References

[1] D. Mozhayeva, C. Engelhard. J. Anal. At. Spectrom., 2020.

[2] M. van der Zande, R.J. Vandebriel, E. Van Doren, E. Kramer, Z. Herrera Rivera, C.S. Serrano-Rojero, E.R. Gremmer, J. Mast, R.J.B. Peters, P.C.H. Hollman, P.J.M. Hendriksen, H.J.P. Marvin, A.A.C.M. Peijnenburg, H. Bouwmeester. ACS Nano, 2012.

[3] M. Witzler, F. Küllmer, K. Günther. Analytical Letters, 2017.

[4] S. Weigel, R. Peters, K. Loeschner, R. Grombe, T.P.J. Linsinger. Anal. Bioanal. Chem., 2017.

[5] F. Loosli, J. Wang, S. Rothenberg, M. Bizimis, C. Winkler, O. Borovinskaya, L. Flamigni, M. Baalousha. Environmental Science: Nano, 2019.

[6] H.E. Pace, N.J. Rogers, C. Jarolimek, V.A. Coleman, C.P. Higgins, J.F. Ranville. Anal. Chem., 2011.

[7] B. Ramkorun-Schmidt, S.A. Pergantis, D. Esteban-Fernandez, N. Jakubowski, D. Günther. Anal Chem, 2015.

[8] M. Sikder, J. Wang, G.T. Chandler, D. Berti, M. Baalousha. Journal of Colloid and Interface Science, 2019.

[9] L. Hendriks, B. Ramkorun-Schmidt, A. Gundlach-Graham, J. Koch, R.N. Grass, N. Jakubowski, D. Günther. J. Anal. At. Spectrom., 2019.

[10] K. Mehrabi, D. Günther, A. Gundlach-Graham. Environmental Science: Nano, 2019.

Contact

icp.info@tofwerk.com