Smart system based on raffinose-coated silver nanoparticles as selective and sensitive optical probe/sorbent for chromium speciation in water samples

P Vasileva[†] [*], L. Djerahov[††], I. Karadjova[†]

[†] Faculty of Chemistry and Pharmacy, University of Sofia "St. Kliment Ohridski", 1164 Sofia, Bulgaria
E-mail : pvasileva@chem.uni-sofia.bg, Karadjova@chem.uni-sofia.bg,
Web page : https://www.uni-sofia.bg

[††] Department of Chemistry, University of Mining and Geology "St. Ivan Rilski", 1700 Sofia, Bulgaria
E-mail : lubomirdjerahov@gmail.com, Web page : http://www.mgu.bg

ABSTRACT

The analytical applications of nanoparticle-assisted smart materials as sensors/sorbents for toxic element speciation have achieved rapid development in recent years [1]. Silver nanoparticles have been already explored as sorbents/colorimetric probes for metal ions determination, but their capabilities for chromium speciation are still not reported [2]. In this study, raffinose-coated silver nanoparticles (Ag@Raff NPs) were successfully applied as both (i) effective sorbent for solid phase microextraction of Cr(III) from aqueous solutions and (ii) optical probe in LSPR based sensing system for quantitative and sensitive determination of Cr(VI).

Ag@Raff NPs with narrow size distribution were synthesized by green ultrasound-assisted reduction method employing raffinose as both reducing and protecting reagent in alkaline reaction medium. UV-visible absorption spectrum of the light yellow aqueous dispersion of Ag@Raff NPs showed surface plasmon resonance band at λ_{max} of 411 nm. The electrostatic surface potential of silver nanoparticles was −47.2±1.1 mV at pH 6.8. The polycrystalline solid product mainly consisted of quasi-spherical silver nanoparticles of mean diameter 27.2±6.7 nm. Some polyhedral nanoparticles were also observed in the TEM micrographs. XRD analysis showed broad diffraction peaks with 2θ of 38.2°, 44.4°, 64.6° and 77.4° corresponding to the (111), (200), (220) and (311) planes, respectively, of the face-centred cubic (fcc) silver (PDF 04-0783).

The analytical method developed for Cr(III) and Cr(VI) determination consists of two steps: (i) Addition of Ag@Raff NPs dispersion to water sample, containing Cr(III) and Cr(VI). Cr(III) is selectively sorbed on the nanoparticle surface under optimized chemical conditions and determined by using ETAAS; (ii) Addition of Ag@Raff NPs dispersion to parallel water sample, containing Cr(III) and Cr(VI). Cr(VI) was in-situ reduced by ascorbic acid to Cr(III) and determined through the sensitive optical response of the silver nanoparticles at optimized ratios between the components and contact time. The calibration curve for Cr(VI) is linear in the range of 2.5-7.5 μmol/L Cr (VI) with quantification limit of 1.9 μmol/L and relative standard deviation from 3% to 5% for the concentration level of 1.9-7.5 μmol/L. Interference studies performed in the presence of various elements showed very good selectivity of Ag@Raff NPs toward Cr(VI).

The added found method was used to confirm accuracy and precision of developed analytical approach. The proposed method was successfully applied for chromium speciation in surface water samples.

Acknowledgements: The authors gratefully acknowledge the financial support provided by Bulgarian Scientific Fund, Grant DN19/10 "Smart Speciation".

REFERENCES

[1] I. Karadjova, T. Yordanova, I. Dakova, and P. Vasileva, "Smart Materials in Speciation Analysis", *Handbook of Smart Materials in Analytical Chemistry*, Vol. 2, pp.757-793,Wiley, (2019).

[2] I. Karadjova, I. Dakova, T. Yordanova, and P. Vasileva, "Nanomaterials for elemental speciation", *J. Anal. At. Spectrom*, Vol. 31, pp. 1949-1973, (2016).