

Investigations of the application of inorganic substrates based on TiO₂ nanocrystals for the detection and quantification of small molecules with SALDI TOF mass spectrometry

I. Popovic¹

¹*Vinca Institute of Nuclear Sciences, Belgrade, Serbia*
e-mail:ivavukicevic@gmail.com

MALDI TOF (Matrix-Assisted Laser Desorption and Ionization Time-Of-Flight) mass spectrometry is soft ionization technique. In order to prevent/reduce fragmentation of analyzed molecules, induced with direct excitation with laser, samples are mixed with matrix molecules. Matrix has high absorption coefficient in the range of the laser emission. In spite of numerous advantages, there are serious drawbacks of the matrices, especially for the analysis of molecules with low molecular mass (above 1000 Da). In this group of molecules there are various biologically active molecules, so there is a great need to overcome disadvantages of the application of organic matrices. Several alternative approaches have been developed: an organic-matrix-free approach in which the substrates, usually nanoparticles act as a matrix.

The term SALDI (Surface-Assisted Laser Desorption and Ionization) was coined to designate the techniques that use nanostructured substrates. Nanoparticles absorb the laser energy and then rapidly transfer to analyzed molecule. Titanium(IV)-oxide (TiO₂) is considered to be a good candidate for SALDI substrate since it is readily available, chemically stable, non-toxic and inexpensive material. TiO₂ is a semiconductor with high absorptivity of UV light of nitrogen laser (have a large band gap 3.2 eV) which is used in MALDI TOF mass spectrometry, but the method of synthesis of TiO₂ nanocrystal have a great impact on absorption because this phenomena depends on size, shape and composition of nanoparticles.

The applicability of TiO₂ nanocrystals of different size and shape was tested. Colloidal TiO₂ nanoparticles, TiO₂ prolate nanospheroids and TiO₂ nanotubes were used as substrates for potential SALDI TOF MS quantitative analysis of biologically active molecules with small molecule mass.

First step to test efficiency of TiO₂ nanocrystal for the mass spectrometry analysis of small molecules was to examine their qualitative characteristics as substrates. It is shown that they have high tolerance to increased concentration on inorganic salts and to high laser intensity. Next step was to examine qualitative characteristics of TiO₂ nanocrystals substrates for mass spectrometric analysis based on following parameters: the homogeneity of the distribution of analyte over substrate surface in SALDI approach define reproducibility and accuracy of the measurement, within day precision to compare the accuracy of measurements with respect to signal intensity and potential use of tested systems for quantitative analysis, and day-to-day reproducibility. Based on all results, the great potential of TiO₂ nanocrystals (especially for the TiO₂ prolate nanospheroids) for the quantitative and qualitative analysis of biologically relevant small molecules (Mm less than 1000 Da) was demonstrated. [1,2,3,4]

REFERENCES

- [1] I. Popovic et al., *Mater. Lett.* 150, 84 (2015).
- [2] I. Popovic et al., *RSC Adv.* 6, 1027 (2016).
- [3] I. Popovic et al., *Opt. Quant. Electron.* 48, 1 (2016).
- [4] I. Popovic et al., *Anal. Bioanal. Chem.* 26, 7481 (2016).