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NANOPARTICLE ENHANCED LASER ABLATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (NELA-ICPMS)

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A sensitivity enhancement methodology for LA-ICPMS based on the surface plasmon resonance phenomenon as a result of metallic nanoparticles (NPs) deposited on the surface of the sample is proposed. Results show that Nanoparticle Enhanced LA-ICPMS (NELA-ICP-MS) increases the sensitivity up to 1 order of magnitude with respect to the conventional LA-ICPMS without any changes of the experimental set up (i.e. laser parameters or gas carrier composition).
Different kind of metallic nanoparticles (AuNPs, AgNPs, PtNPs) and substrates (metallic and dielectric -Cu, Cu-based alloys, Ti, glass, Si-) were tested.
The enhancement depends on both dropped nanoparticles (kind, concentration and size) and sample tested (investigated element and matrix). Metallic elements show enhancement in both conductive and dielectric matrices, although the better results are obtained on conductive matrix. Different elements show different enhancement in the same matrix, as well as the same element shows different enhancement in different matrices.
Differences in morphology and depth of the craters produced by the laser pulse in the presence and in the absence of NPs, as well as the different size and composition of laser-generated particles allow to attribute to a different laser-substrate interaction the observed enhancement.
In particular, NPs induce locally more efficient ablation below the ablation threshold, that leads to the formation of smaller laser-generated particles, consisting of target material aggregated around NPs, that exhibit better transport/vaporization efficiency, thus enhancing signals for metallic samples.
NPs do not contaminate the sample irreversibly because, after a very limited number of laser shots, they are completely removed from the sample surface.

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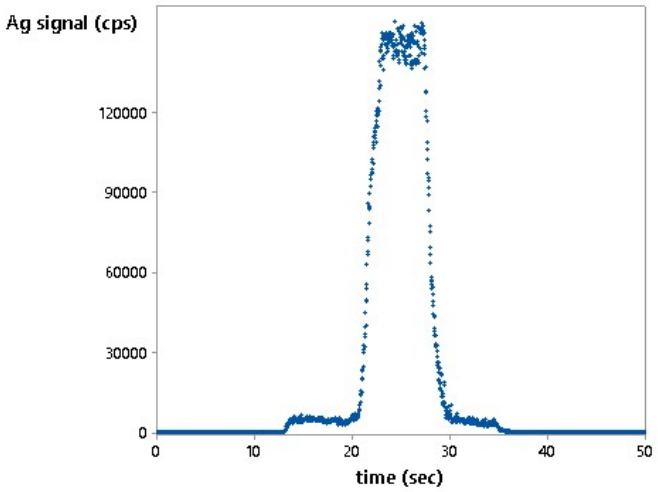

Figure 1. Line analysis of Ag on pure Copper with a 100 µm diameter circular beam at 500 µm/s ablation rate. Laser ablation started 2 mm before (13-20 sec) and stopping 2 mm after (30-35 sec) NPs drop (20-30 sec). PtNPs 17 nm sized, [PtNPs] = 66 fmol/ mm^2

The method developed allows to obtain the same intensity signal as traditional LA-ICPMS by strongly reducing the number of laser pulses on samples, making the technique more suitable for analyses in which negligible destructivity and/or determination of surface-distribution patterns of very thin layers without underlying contamination are demanded. Moreover, it can be particularly useful to cut down isobaric interference (i.e. Cr and Mn interfered by ArO and ArN) because it allow to increase the analyte signal without increasing the interferences, so increasing signal to noise ratio.
The undoubted strength of this approach is represented by its simplicity, affordability and fast performance.