PO-TS-05: CAPILLARY LC OF METALLIC NANOPARTICLES COUPLED ON LINE TO IT-SPME: APPLICATION TO PLASMONIC ASSAYS.

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The use of metallic nanoparticles, in particular Ag and AuNPs has increased in the last years, and so their impact on the environment and human healthy is nowadays a topic of concern. A variety of methods has been proposed to characterization and quantify NPs, however most of them are based on indirect estimations to estimate their concentrations. Therefore, the development of new analytical tools to determine metallic NPs is of utmost importance.

Recently, in-tube solid-phase microextraction coupled to capillary liquid chromatography with diode array detection (IT-SPME Cap-LC-DAD) has been proposed a new tool for estimating mean concentrations of Ag/AuNPs [1], and thereby determine their average size. Size-exclusion and hydrophobic effects are the mechanisms involved to explain the chromatographic profiles of the nanoparticles (Figure 1). Table 1 shows the average sizes estimated for several naked AuNPs from the relationship between area of the two peaks as an analytical signal. Moreover, the results have been compared with other techniques (DLS and TEM) showing that the chromatographic analytical signal responds to the hydrodynamic diameter (Figure 2).

The proposed technique allows the direct analysis of AuNPs in different matrices, providing new information for their characterization.

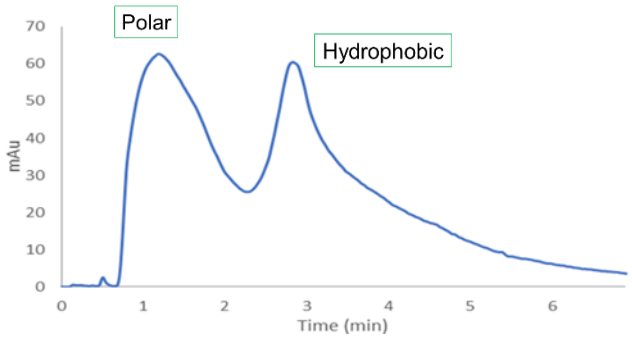

Figure 1: Chromatographic profile of naked AuNP aqueous dispersions.

Table 1: Hydrodynamic diameter of different naked AuNPs synthesis estimated by IT-SPME-Cap-LC-DAD.

NPs	Synthesis A	Synthesis B	Synthesis C	Synthesis D	Synthesis E
Diameter (nm)	17.47	15.85	16.15	16.44	22.06

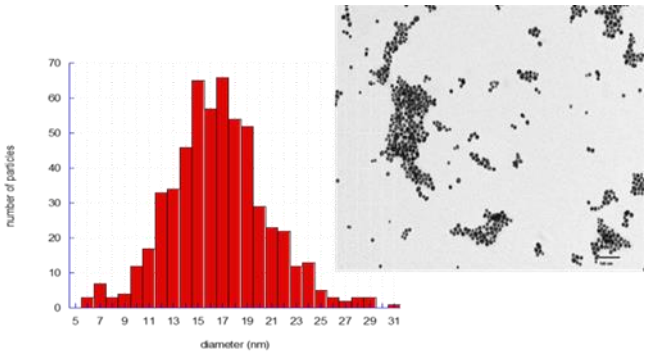

Figure 2: AuNP's hydrodynamic diameter. Attached TEM image and distribution histogram of NPs (DLS).

In this work, the possibilities of IT-SPME Cap-LC-DAD for aggregated AuNPs have been evaluated. As an

example, the espermine colorimetric assay previously developed by this research group is addressed [2].

Figure 3 shows the variation of the chromatographic profiles as a function of the target analyte concentration, showing a decrease in chromatographic peak at t_R = 2.93 min.

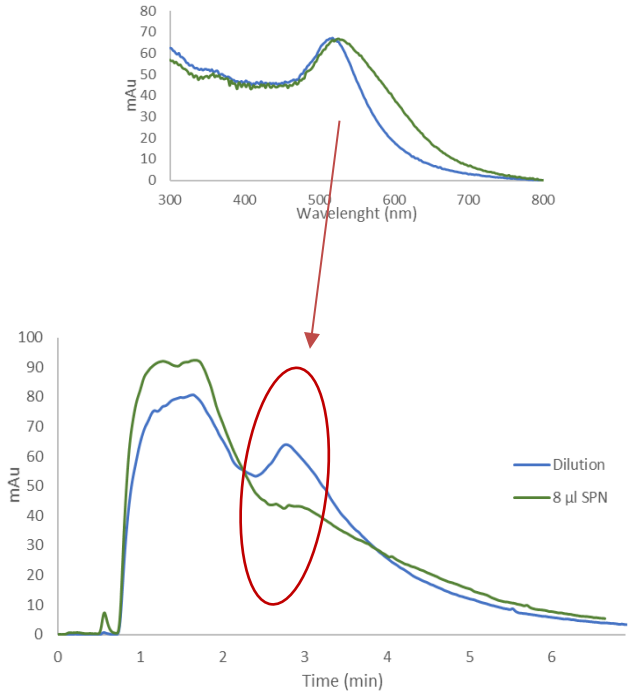

Figure 3: Chromatographic profiles of spermine assay. Inset: UV-Vis spectra associated to the chromatogram at t_R= 2.93 min.

The absorption spectra of AuNPs showed a correlation with the chromatographic profiles of different solutions.

The practical application of the methodology was carried out by analyzing urine samples following the procedure described below.The samples were treated by solid phase extraction in C_{18} silica cartridges [3]. First, C_{18} silica cartridges were conditioned with methanol and hydrogen carbonate solution at pH 12. Then, 1 mL of urine or of urine spiked with SPN was passed through the cartridge. Then, hydrogen carbonate solution, acetonitrile, and nanopure water were used to wash the sample. Finally, polyamines were eluted with AcOH 5% in two fractions of 0.25 mL each.

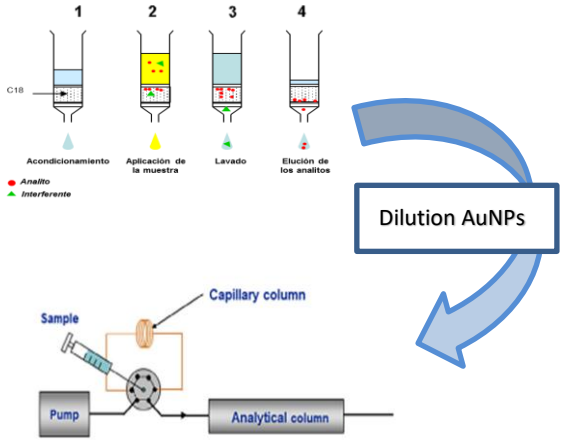

Figure 4: Solid phase extraction methodology for treated of samples and injection the NPs in the chromatographic system

Results indicated that the behavior of spermine in urine samples were comparable to the behaviour achieved in water satandards, showing a variation in the chormatographic profiles. Therefore, IT-SPME Cap-LC-DAD is a potential application to the investigation in clinical analysis.

Acknowledgements

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