

Área: **FIS**

TiO₂ nanotubes films decorated with Ag nanoparticles as SERRS substrate for determination of anthocyanins species in grape skin at different pH values.

Gabrielle Sarto (PG)^{1*}, Thiago N. M. Cervantes (PQ)¹, Lucio C. Almeida (PQ)^{1*}

***gabriellesarto@uel.br; *lucioalmeida@uel.br**

¹Laboratory of Environmental Electrochemistry – LabEA, Department of Chemistry, Londrina State University (UEL), Londrina, PR - Brazil.

Palavras-Chave: TiO₂NTs, AgNPs, Anthocyanins

Highlights

SERRS substrate promoted a signal intensification for anthocyanins species in different pH.

Versatile and promising platform for SERRS speciation of anthocyanin species present in the grape extracts.

Abstract

Anthocyanins are natural dyes widely used in the food industry. They occur in various natural sources and are primarily responsible for the coloration of many cultivars, notably grape skins [1]. In aqueous medium, anthocyanins are present in equilibrium among four different species, depending on the pH medium. Under acidic conditions, the solution displays a reddish color due to the predominance of the flavylium cation (i.e., cationic form of anthocyanin). At pH values above 4, the quinoidal base becomes predominant, resulting in a bluish coloration [2]. In this context, the present study proposes the development of a SERRS (Surface-Enhanced Resonance Raman Scattering) sensor for anthocyanin speciation as a function of pH values. This sensor is based on titanium dioxide nanotubes (TiO₂NTs) films obtained by electrochemical anodization and decorated with colloidal silver nanoparticles (AgNPs). Electrochemical anodization occurs in three stages: two anodization using 30 V for 24 h and one anodization of 30 V for 30 min to obtain self-detachment of TiO₂NTs. The films were placed on a glass substrate, and samples were prepared using 5 μL of grape peel extract diluted to 1% and 5 μL of AgNPs colloidal solution. The pHs of the extracts were 3, 4, 5, 6, 7, and 8. UV-Vis spectroscopy was employed to identify the anthocyanin species in response to pH variation. Raman spectral analysis revealed a pronounced SERRS effect only in the presence of AgNPs, confirming the enhancement of anthocyanin vibrational modes onto TiO₂NTs/AgNPs substrate. The preliminary results have shown an enhancement factor (EF) from 10⁵ to 10⁶, considering the main bands related to anthocyanin. Deconvolution of the SERRS spectra also enabled the evaluation of the relative proportions of the flavylium cation and the quinoidal base at different pH values, as well as their interaction with the substrate. This study revealed the potential of TiO₂NTs films decorated with AgNPs as an effective SERRS sensor for monitoring the anthocyanin composition in real samples of grape skin extracts as a function of pH, without prior preparation, allowing their detection at low concentrations.

[1] Sarto G et al., **Vibrational Spectroscopy** vol. 134, 103716 (2024)

[2] Zaffino C.; Russo B.; Bruni S., **Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy**, vol. 149, 41-47 (2015).

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