Solid-Phase Extraction with Alginate-Encapsulated Hydrophobic Deep Eutectic Solvent for Copper Pre-Concentration in Saliva Prior to FAAS analysis

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Highlights

- HDES-encapsulated in alginate for solid-phase extraction (SPE) for method.
- Enhanced sensitivity for Cu determination by FAAS.
- A non-invasive approach to detect Cu levels in saliva.

Abstract

Copper (Cu) performs essential functions in the human body, acting as an enzyme cofactor, aiding cellular energy production, and playing a fundamental role in general metabolism. However, variations in copper levels can indicate disorders and illnesses, such as Wilson's Disease (WD). This genetic condition causes copper accumulation into the brain, kidneys, liver, and eyes due to the body's inability to metabolize the metal. Currently, WD is diagnosed by laboratory tests (e.g., blood or urine tests) and liver tissue biopsies. These methods can be invasive and uncomfortable for patients, making saliva a strategic sample. In patients with WD, Cu concentrations in saliva are higher than 300.2 µg L^{-1}. This study addresses the application of hydrophobic deep eutectic solvents (HDES) encapsulated into alginate capsule for the Cu extraction in saliva samples, allowing preconcentration of the analyte and improving sensitivity in determinations by flame atomic absorption spectrometry (FAAS). HDES are sustainable, biodegradable, and tunable solvents that can be applied in extraction methods for trace elements. However, the direct addition of HDES to the sample proved unfeasible due to the formation of an emulsion and incompatibility with the FAAS sample introduction system. To overcome this problem, HDES encapsulated in alginate capsule were evaluated for the SPE of Cu in saliva samples. To develop the method, 1.0 mL of a saliva sample was digested with 1.0 mL of 6% H_2O_2 v v^{-1} in an ultrasound bath (10 min at 70 °C). Additionally, 100 mg of the HDES solid-phase was added to 2.0 mL of the 1:1 sample:H_2O_2 mixture, followed by extraction for 6 min under vortex shaking. The liquid phase was then discarded, and 0.50 mL of 5% v v^{-1} HNO_3 was used for analyte elution in a final volume of 500 µL before determination by FAAS. This method achieved a 2-fold pre-concentration factor in Cu determination. Analyte addition and recovery tests (250 µg L^{-1}) achieved recovery values of 100%. The method will be applied to samples from patients diagnosed with WD, providing a fast, simpler, and greenness sample preparation method. The developed method is based on the principles of Green Analytical Chemistry, once the analytical greenness metric for sample preparation (AGREEprep), achieved scores greater than 0.51. This method uses sustainable solvents and generates a minimal amount of hazardous chemical waste. Furthermore, this work contributes to achieving the 3, 9, 12, and 14 United Nations' Sustainable Development Goals (SDGs).

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