

Sustainable Strategy Using Deep Eutectic Solvents for Multi-Matrix Sample Analysis by MIP-OES

Floriatan S. Costa (PQ)^{1,2,*}, Samara G. Banhos (PG)^{1,3}, Marcelo L. L. Tozo (PG)^{1,3}, Mariana E. M. Araújo (IC)², Mateus O. Müller (PG)², Mario H. Gonzalez (PQ)⁴, Clarice D. B. Amaral (PQ)², Ana Rita A. Nogueira (PQ)^{1,3}

*floriatancosta@ufpr.br

¹Embrapa Pecuária Sudeste, São Carlos, SP, Brasil; ²Department of Chemistry, Universidade Federal do Paraná, Curitiba, PR, Brasil; ³Applied Instrumental Analysis Group, Universidade Federal de São Carlos, São Carlos, SP, Brasil;

⁴Department of Chemistry and Environmental Science, Universidade Estadual Paulista, São José do Rio Preto, SP, Brasil.

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Highlights

- DES was applied in sample preparation for multi-elemental determination in multi-matrix samples.
- Optimal conditions are achieved using the Doehlert design.
- A new, efficient, and sustainable DES-based application was developed.

Abstract

Sample preparation is a critical step in analytical chemistry due to the complexity and variability of sample matrices. Despite recent advances, further improvements are needed, particularly in developing more sustainable approaches aligned with Green Sample Preparation (GSP) principles.⁽¹⁾ In this context, this study investigated the use of deep eutectic solvents (DES) in extraction methods for multi-matrix sample analysis. DES is an environmentally friendly and tunable solvent with advantageous chemical properties for organic and inorganic sample preparation. The DES was prepared by combining choline chloride (ChCl) with various carboxylic acids in a 1:1 molar ratio, including acetic acid (AA), formic acid (FA), malonic acid (ML), malic acid (MA), and oxalic acid (OX). These solvents were used to extract Ca, K, Mg, Mn, and Na from certified samples of plant and animal tissues, soil, mineral fertilizer (phosphate rock), and rice flour. Experimental conditions were optimized by considering the type and composition of the DES, as well as parameters such as solvent volume and extraction time, using a Doehlert design. The procedure was performed using a heating block, followed by elemental determination via microwave-induced plasma optical emission spectrometry (MIP-OES). Various DES compositions were tested, and method performance was evaluated based on % recovery relative to reference values. In the evaluation of DES composition, ML showed the highest efficiency for plant, soil, and mineral rock samples, while FA was more suitable for fish tissue and AA for rice flour. Additionally, the effect of water addition to the DES composition was evaluated, demonstrating increased extraction efficiency, especially for inorganic matrices (e.g., soil and mineral fertilizer). The optimization of extraction time (min) and solvent volume (mL) allowed for the determination of the most favorable conditions, resulting in robust statistical models ($R^2 > 0.945$). The optimal conditions were 2 to 3 mL of DES, with extraction times ranging from 50 to 85 min, providing high % recovery for all analytes. The method's trueness was confirmed using certified reference values (% recovery ranging from 88% to 105%), and a spiking experiment conducted at three concentration levels (2, 5, and 10 mg L⁻¹), yielding recoveries between 95% and 111%. The method's repeatability was satisfactory ($n = 8$), with relative standard deviations below 8.6%. The results highlight the efficiency of DES in extraction procedures that utilize simpler approaches and accessible instrumentation. Moreover, the developed methods demonstrated strong performance in sustainability evaluation using the analytical greenness metric for sample preparation (AGREEprep),⁽²⁾ achieving scores greater than 0.60. This study establishes DES as a green alternative for multi-matrix elemental analysis, offering improved efficiency and sustainability in sample preparation. Additionally, this work contributes to the achievement of the United Nations' Sustainable Development Goals 12, 13, and 15.

¹ López-Lorente et al., *TrAC Trends Anal. Chem.*, 2022, 148, 116530.

² Costa, et al., *TrAC Trends Anal. Chem.*, 2024, 174, 117677.

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