

Surfactant-Assisted Extraction of Trace Metals from Sedimentary Rocks As A Green Alternative To Acid Digestion Prior To Icp-Oes Determination

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ABSTRACT

Diabetes mellitus remains a major metabolic disorder requiring safer and affordable therapeutic alternatives. This study evaluated the safety profile, in vitro antidiabetic activity, and phytochemical composition of a formulated polyherbal syrup (PHS) prepared from *Vernonia amygdalina*, *Moringa oleifera*, *Zingiber officinale*, *Allium cepa*, and *Allium sativum*. Aqueous extracts of onion, garlic, and ginger were obtained by decoction of 20 g powdered samples in 100 mL distilled water at 40 °C for 3 h, while fresh leaves of *Moringa oleifera* and *Vernonia amygdalina* were extracted by manual juice expression and filtration. The extracts were combined with honey to produce the polyherbal syrup. Acute toxicity evaluation in albino rats using oral doses of 1000–16000 mg/kg body weight revealed no mortality or visible signs of toxicity, indicating an LD₅₀ greater than 16000 mg/kg. Sub-acute toxicity studies conducted at doses of 25–400 mg/kg also showed no adverse behavioural or physiological changes. In vitro antidiabetic assays revealed that PHS is concentration-dependent. The PHS exhibited IC₅₀ values (µg/mL) of 8.88 for glucose uptake, 2.55 for α-amylase inhibition, and 3.50 for α-glucosidase inhibition, compared with the standard drug acarbose which showed IC₅₀ values of 3.55, 1.89, and 3.39 µg/mL respectively. Although the standard drug showed slightly higher potency, the PHS demonstrated comparable α-glucosidase inhibitory activity. GC–MS profiling revealed numerous bioactive phytochemicals including 2,3-dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one, 5-hydroxymethylfurfural, thymine, n-hexadecanoic acid, and octadec-9-enoic acid. The combined presence of these compounds suggests possible synergistic pharmacological interactions responsible for the observed antidiabetic effects. These findings indicate that the formulated polyherbal syrup is safe and possesses promising antidiabetic potential.

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INTRODUCTION

Trace metals in sedimentary rocks provide valuable information on geological processes, environmental conditions, and anthropogenic influences. Elements such as Mn, Zn, Ni, and Co are essential at trace levels but may become environmentally significant when enriched, whereas Pb is recognized for its toxicity even at low concentrations. Because sedimentary rocks act as long-term repositories of these elements, their characterization is important for geochemical investigations, environmental assessments, and resource evaluation (Llaver *et al.*, 2021).

Accurate determination of trace metals in geological materials generally requires sample decomposition prior to instrumental analysis. Conventional procedures, including EPA 3050B and related acid digestion methods, employ concentrated mineral acids, elevated temperatures, and extended preparation times. Although effective, these approaches generate hazardous wastes, increase operational costs, and are not fully aligned with the principles of green analytical chemistry (Nemček and Hagarová, 2021). Consequently, considerable effort has been directed toward developing alternative sample preparation strategies that reduce acid consumption while maintaining analytical reliability.

Among such alternatives, surfactant-based extraction systems have attracted attention because of their ability to enhance analyte solubilization and mass transfer. Surfactant-based extraction techniques, particularly cloud point extraction

(CPE), have emerged as promising environmentally friendly alternatives for trace metal preconcentration. Non-ionic surfactants form micellar systems capable of solubilizing hydrophobic metal complexes and enabling efficient phase separation (Korn *et al.*, 2006; Bezerra *et al.*, 2011; Sznec *et al.*, 2025). These approaches have been successfully applied to aqueous environmental samples (Akiba *et al.*, 2021; Mouco-Novegil *et al.*, 2023; Garoub & Gouda, 2022). However, their application to solid geological matrices remains limited due to the rigidity and complexity of mineral structures, which restrict efficient metal release.

Beyond micellar solubilization, surfactants reduce interfacial tension and improve wetting, thereby facilitating penetration into porous materials and promoting the desorption of matrix-associated species (Rosen and Kunjappu, 2012). Applications to solid matrices have been reported mainly for soils, sewage sludge, and contaminated sediments, where surfactants assist the mobilization of surface-bound contaminants. However, these studies generally target loosely bound species and do not address the extraction of trace metals from consolidated geological materials.

The extension of surfactant-assisted extraction to sedimentary rocks remains largely unexplored. Unlike soils and unconsolidated sediments, sedimentary rocks possess compact mineral frameworks in which trace metals may be incorporated within carbonate, clay, or silicate phases during weathering, deposition, and diagenetic processes (Plank, 2014; Rollinson and Pease, 2021). Consequently, the release

of these elements is often more challenging than in loosely consolidated matrices, and simple surfactant leaching may not provide sufficient analyte recovery. While surfactants are known to improve wetting, interfacial contact, and mass transfer in porous materials (Rosen and Kunjappu, 2012), their potential application as extraction media for consolidated geological materials has received little attention. We hypothesized that combining the wetting and penetration properties of non-ionic surfactants with controlled hydrothermal treatment could enhance access to internal pore networks and mineral interfaces, thereby promoting metal release without extensive use of strong acids. To our knowledge, the use of surfactant media as the primary extraction environment for trace-metal determination in consolidated sedimentary rocks under sealed hydrothermal conditions has not been systematically investigated. Therefore, this study evaluates a surfactant-assisted hydrothermal extraction procedure employing non-ionic surfactants in PTFE-lined vessels for the determination of Ni, Pb, Zn, Mn, and Co in sedimentary rock samples prior to ICP-OES analysis. The analytical performance of the proposed method was assessed in terms of extraction efficiency, precision, and accuracy, and compared with that of a conventional acid digestion procedure. The work explores the feasibility of a reduced-acid approach for trace-metal determination in complex geological matrices while contributing to the development of greener sample preparation methodologies.

MATERIALS AND METHODS

Instrumentation

Trace metal concentrations were determined using an Optima 7000 DV inductively coupled plasma optical emission spectrometer (ICP-OES, PerkinElmer, USA) operated under optimized conditions: RF power 1300 W, plasma gas flow 15 L min⁻¹, auxiliary gas flow 0.2 L min⁻¹, nebulizer gas flow 0.8 L min⁻¹, and sample uptake rate 1.5 mL min⁻¹. Measurements were performed in axial view mode with three replicate readings.

Optimization of Extraction Variables

Extraction parameters, including surfactant type and concentration (2–7% w/v), pH (2–8), extraction temperature (40–200 °C), extraction time (0.5–3 h), and centrifugation time (5–15 min), were optimized using a one-variable-at-a-time approach. Optimal conditions were selected based on maximum analytical response and efficient phase separation. Although multivariate experimental designs can provide information on factor interactions, the present study was intended as an initial feasibility assessment of surfactant-assisted extraction for consolidated sedimentary rock matrices. Consequently, a univariate optimization strategy was adopted to establish the principal operating conditions prior to future multivariate investigations. Because this short communication focuses on method feasibility and extraction performance, preconcentration factor evaluation was beyond the scope of the current study, and the previously included equation has therefore been removed.

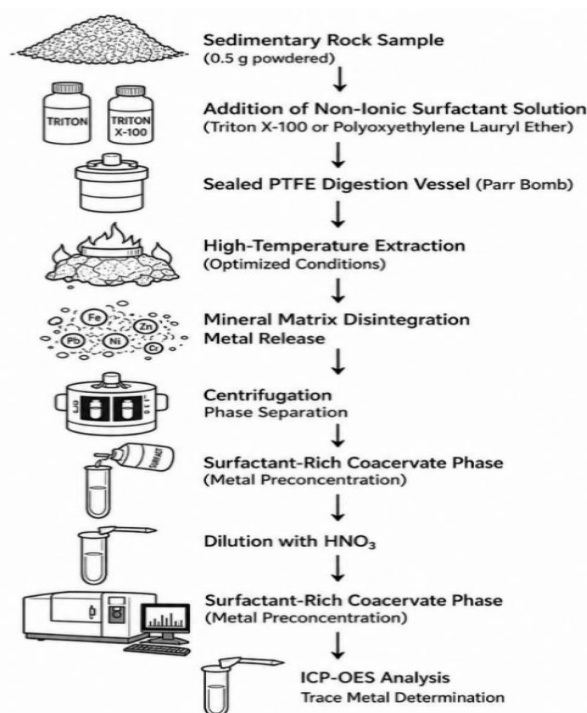


Figure 1: Schematic Representation of the Surfactant-Assisted Extraction Procedure Used for Trace Metal Determination in Sedimentary Rocks Prior to ICP-OES Analysis

Surfactant-Assisted Extraction Procedure

For surfactant-assisted extraction, 0.5 g of powdered sedimentary rock was transferred into PTFE-lined Parr extraction vessels and mixed with 15 mL of an aqueous 5% (w/v) non-ionic surfactant solution. The pH was adjusted using dilute HNO₃ or NaOH. Based on univariate optimization, Triton X-100 was used at pH 5.5 and an extraction temperature of 105 °C for Mn and Co, whereas

polyoxyethylene lauryl-10-ether was used at pH 7.6 and an extraction temperature of 180 °C for Ni, Pb, and Zn. The sealed vessels were heated at a rate of 5 °C min⁻¹ to the target temperature and maintained for 1.5 h under autogenous pressure before being allowed to cool naturally to room temperature. Pressure was not directly monitored and corresponded to the autogenous pressure generated within the sealed vessels at the selected operating temperatures.

The resulting suspensions were centrifuged at 3200 rpm for 11 min to achieve phase separation. The surfactant-rich coacervate phase was isolated, diluted to 10 mL with 2% (v/v) HNO₃ to reduce viscosity, and analyzed directly by ICP-OES. Procedural blanks and triplicate extractions were included throughout. Although the extraction was conducted in sealed vessels, the method substantially reduced the use of concentrated mineral acids compared with conventional digestion procedures and therefore represents a lower-waste alternative for trace metal extraction from sedimentary rock matrices.

Reference Acid Digestion Method

For comparison, samples were also processed according to EPA Method 3050B. Briefly, 0.5 g of sample was treated sequentially with HNO₃, H₂O₂, and HCl under controlled heating conditions. The resulting digest was filtered, diluted to 100 mL with ultrapure water, and analyzed by ICP-OES.

Instrumental Analysis and Method Validation

To minimize physical interferences associated with the surfactant-rich matrix, all calibration standards were prepared using matrix-matched solutions containing surfactant concentrations comparable to those present in the final diluted sample extracts. This approach ensured similar nebulization and sample transport characteristics between standards and samples. Analytical performance was evaluated in terms of linearity, limits of detection (LOD), limits of quantification (LOQ), precision, and accuracy. LOD and LOQ were calculated as $3\sigma/m$ and $10\sigma/m$, respectively, where σ is the standard deviation of the blank and m is the slope of the calibration curve. Precision was expressed as relative standard deviation (RSD), while accuracy was assessed through recovery studies. Statistical comparison of results obtained from the surfactant-assisted extraction and EPA 3050B methods was performed using a paired t-test at a 95% confidence level. While spike-recovery studies were used to evaluate method feasibility, the absence of certified reference material (CRM) validation is acknowledged as a limitation of

the present study and should be addressed in future investigations.

RESULTS AND DISCUSSION

Surfactant-Mediated Extraction Performance

The surfactant-assisted extraction procedure successfully recovered trace metals from sedimentary rock matrices under the optimized experimental conditions. Extraction performance increased with surfactant concentration up to approximately 5% (w/v), beyond which no substantial improvement was observed. This behavior is consistent with cloud-point extraction systems, where increasing surfactant concentration enhances micelle formation and analyte incorporation but may eventually reduce extraction efficiency due to increased solution viscosity and impaired phase separation (Korn *et al.*, 2006; López-Darias *et al.*, 2008).

The concentrations reported in Table 1 correspond to a representative sedimentary rock sample analyzed under the optimized extraction conditions and are expressed as mean \pm standard deviation of three independent extractions. Method performance was evaluated through spike-recovery experiments and comparison with EPA 3050B partial digestion. However, certified reference materials were unavailable; therefore, absolute accuracy could not be independently verified.

The optimized conditions demonstrated that extraction performance depended on both surfactant type and extraction temperature. Polyoxyethylene lauryl-10-ether produced higher analytical responses for Ni, Pb, and Zn at 200 °C, whereas Triton X-100 was more effective for Mn and Co at 100 °C. Although the mechanism underlying this selectivity was not investigated in the present study, the observed differences may be related to variations in metal speciation, mineral associations, and interactions within the surfactant-rich phase (López-Darias *et al.*, 2008). These findings suggest that metal-specific extraction conditions are required to maximize analytical response in sedimentary rock matrices, and further studies are needed to elucidate the mechanisms responsible for the observed selectivity.

Table 1: Optimum Concentration of Surfactant, Temperature and Time and the Concentration of Each Metal Extracted

Metals	Surfactant (5%)	Time (h)	pH	Centrifugation Time (mins)	Temperature (°C)	Concentration $\mu\text{g/g}$
Ni	polyoxyethylene lauryl-10-ether	1	7.6	11	200	449 \pm 0.21
Pb	polyoxyethylene lauryl-10-ether	1	7.6	11	200	1173 \pm 3.10
Zn	polyoxyethylene lauryl-10-ether	1	7.6	11	200	1593 \pm 5.09
Mn	Triton X-100	1	5.5	11	100	669 \pm 0.26

Influence of Physicochemical Conditions

Solution pH and extraction temperature significantly influenced metal recovery. Optimal responses were obtained within the mildly acidic to near-neutral pH range (5.5–7.6). Outside this range, extraction performance declined, possibly due to changes in metal speciation, competition effects, or precipitation phenomena that reduce transfer into the surfactant-rich phase. Similar pH-dependent behavior has been reported in surfactant-assisted and cloud-point extraction systems (Korn *et al.*, 2006; Yazdi, 2011).

Temperature also played a critical role in extraction performance. Increased temperatures promoted phase separation and facilitated extraction above the cloud point of the surfactants, leading to more efficient coacervate formation. The elevated temperatures employed within the sealed PTFE-lined vessels may additionally have enhanced contact between the extraction medium and the sedimentary

rock matrix, thereby improving analyte release. However, excessively high temperatures did not yield further improvements, indicating the importance of controlled extraction conditions.

Analytical Performance and Method Reliability

The proposed method exhibited good analytical performance, with calibration linearity exceeding $R^2 = 0.999$ for all analytes, limits of detection ranging from 0.08 to 0.42 $\mu\text{g g}^{-1}$, and relative standard deviations below 5%. Spike recoveries ranged from 72 to 85%, indicating moderate but reproducible recovery of trace metals from the sedimentary rock matrix. Such recoveries are reasonable for complex geological materials in which analytes may be strongly associated with mineral phases and therefore not completely released during extraction.

Although method accuracy was assessed through spike-recovery experiments and comparison with EPA 3050B, the absence of certified reference material validation remains a limitation of the present study. Consequently, the analytical performance reported here should be regarded as demonstrating method feasibility rather than definitive validation for all geological matrices.

Comparison with EPA 3050B Acid Digestion

Comparison with EPA 3050B revealed higher measured concentrations for Ni, Pb, Zn, and Mn in the surfactant-assisted extracts, whereas Co showed lower recovery. These results indicate that the two procedures access or quantify metals differently within the sedimentary rock matrix. However, in the absence of certified reference materials or total digestion data, the higher concentrations obtained by the surfactant-assisted procedure should not be interpreted as evidence of superior extraction efficiency. Differences may arise from variations in analyte release from mineral phases,

partitioning behavior into the surfactant-rich phase, and potential matrix-related effects during instrumental determination. Similar cautions regarding interpretation of partial extraction comparisons have been widely reported in analytical geochemistry studies (Rollinson and Pease, 2021; Nemček and Hagarová, 2021).

A notable advantage of the proposed method is the substantial reduction in the use of concentrated mineral acids. Unlike EPA 3050B, which requires multiple strong acids for digestion, the surfactant-assisted procedure employs only dilute acid for pH adjustment and final dilution, thereby reducing reagent consumption and hazardous waste generation. This aligns with the principles of green analytical chemistry. Nevertheless, the method should be regarded as a surfactant-assisted extraction approach rather than a total digestion technique, and its applicability will depend on the mineralogical form and distribution of the target metals within the geological matrix.

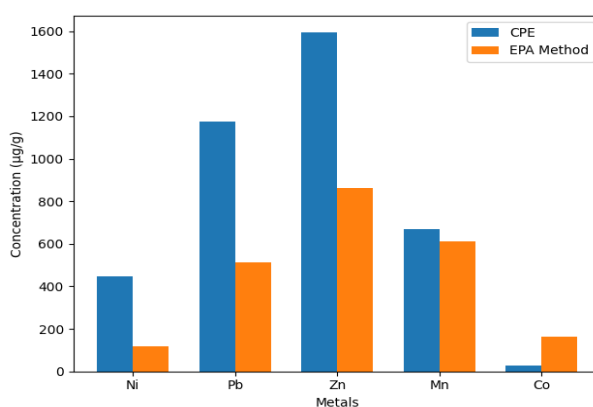


Figure 2: Comparative Extraction Performance of Surfactant-Assisted Extraction and EPA 3050B Acid Digestion

Figure 2 shows the comparative extraction performance of surfactant-assisted extraction and EPA 3050B acid digestion for trace metals (Ni, Pb, Zn, Mn, and Co) in sedimentary rock samples, as determined by ICP-OES. The surfactant-based approach demonstrates higher measured concentrations for Ni, Pb, Zn, and Mn, reflecting analyte enrichment within the surfactant-rich phase and potentially reduced matrix-related interferences during instrumental determination.

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