Brazilian Journal of Analytical Chemistry
***Pre-publication – Accepted after peer review***
doi: 10.30744/brjac.2179-3425.AR-10-2025

***ARTICLE***

# Vortex-Assisted Liquid-Liquid Microextraction Based on Hydrophobic Deep Eutectic Solvent for Nickel Determination in Water Samples by Smartphone Digital Image Colorimetry

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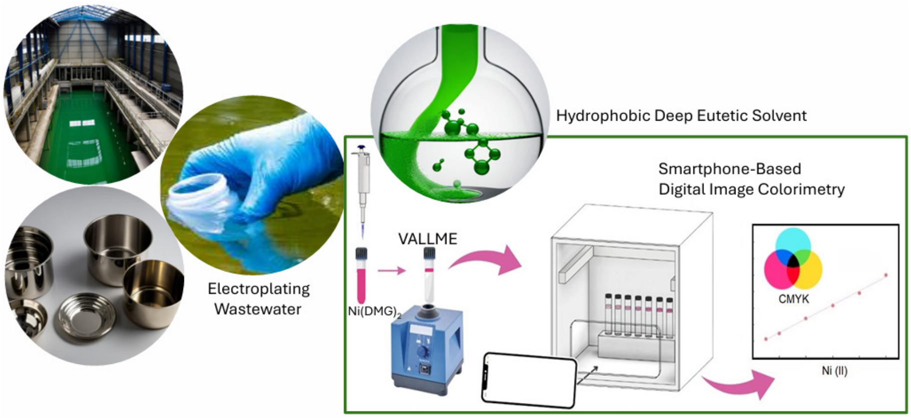

An environmentally friendly and sensitive vortex-assisted liquid-liquid microextraction (VALLME) method using a hydrophobic deep eutectic solvent (HDES) coupled with smartphone-based digital image colorimetry (SDIC) was developed for the preconcentration and determination of trace nickel in electroplating wastewater. Nickel cations were complexed with dimethylglyoxime (DMG) to form a pink-red complex ($Ni(DMG)_2$). Some important factors, including the HDES type, pH, volume of solvent, dimethylglyoxime concentration, and vortex time, were investigated and optimized. The extraction was performed in 1 minute using 250 µL of HDES composed of tetrabutylammonium bromide (TBABr) with decanoic acid (1:2), with a sample volume of 10 mL at pH 8, and the image capture was made directly in the extraction tube without the need to separate the HDES phase. Under the optimum conditions, the method exhibited linearity within the concentration range of 0.45-5.9 mg $L^{-1}$, detection and quantification limits of 0.15 and 0.45 mg $L^{-1}$, and precision (RSD) of ± 2.6%. Application to water samples showed recoveries between 97% and 104%. The proposed HDES-based microextraction method offers an effective alternative for nickel determination in industrial wastewater.

**Keywords:** nickel, liquid-liquid microextraction, deep eutectic solvent, water samples, electroplating

**Cite:** Pereira, A. V.; Fatibello-Filho, O.; da Penha, G. M.; Tavares, E. A. Vortex-Assisted Liquid-Liquid Microextraction Based on Hydrophobic Deep Eutectic Solvent for Nickel Determination in Water Samples by Smartphone Digital Image Colorimetry. *Braz. J. Anal. Chem.* (Forthcoming). http://dx.doi.org/10.30744/brjac.2179-3425.AR-10-2025

Submitted March 1, 2025; Resubmitted April 25, 2025; Accepted May 21, 2025; Available online June, 2025.

## INTRODUCTION

Ensuring universal access to drinking water is currently a sustainable global development goal.[1] However, water source contamination by numerous pollutants, both biological and chemical, due to various human activities, including urban development, inadequate waste disposal, industrial processes, and agricultural practices, impacts the environment and poses major health hazards to people.[2]

Heavy metal pollution has emerged as a critical global issue due to its high toxicity, bioaccumulation, and non-biodegradable nature.[3] Similarly to many other heavy metals, nickel is a naturally occurring element found in the soil and water. It is released into the atmosphere from natural sources, and low levels are present in fresh water, seawater, and groundwater.[4,5] However, anthropogenic activities such as burning fossil fuels, mining, metal processing and casting, and electroplating wastewater may elevate nickel levels in the environment.[6]

Apparently, the oral toxicity of nickel is low due to poor intestinal absorption when ingested with food; however, a higher percentage is absorbed when nickel cations are dissolved in water.[7] Fortunately, animal tissues rarely accumulate nickel compared to other heavy metals like lead, arsenic, and cadmium.[8] Nevertheless, depending on dose and exposure time, intake of nickel ions could potentially impact health. It is a potential carcinogen to the respiratory tract and can cause toxic effects, such as cardiovascular disease, asthma, and lung fibrosis.[4,9] Additionally, skin contact with stainless steel or nickel-plated objects (e.g., earrings, jewellery, orthodontic wires and appliances) and using cosmetics with nickel traces can cause allergic contact dermatitis.[6]

Environmental regulations play an important role in reducing water contamination by establishing standards for water quality. In Brazil, the National Environment Council (CONAMA), through resolution 357/2005, has set maximum allowed levels for several pollutants, including nickel, in various surface water bodies (freshwater, saltwater, brackish water, and effluent release).[10] According to the CONAMA resolution, the maximum allowable concentrations of nickel are 25 µg $L^{-1}$ and 2.0 mg $L^{-1}$ for freshwater and wastewater, respectively. One of the key challenges in monitoring and preventing metal contamination in water is the development of sensitive, reliable, and rapid methods for detecting heavy metals in water bodies.

Determination of trace nickel is usually based on traditional techniques such as flame atomic absorption spectrometry (FAAS),[11,12] HPLC UV-Vis with derivatization reagent,[13,14] differential pulse polarograpy,[15] voltammetry,[16] fluorimetry,[17] and spectrophotometry.[18-20] However, some of these methodologies have limitations, including time-consuming procedures, sophisticated equipment, and consumption of large amounts of solvents. Also, they are not portable for in situ analysis.

Among the numerous methods proposed for nickel determination, colorimetric procedures have some advantages, such as easy execution, low cost, and sensitivity. Oxime ligands such as dimethylglyoxime[21] and α-furildioxime[19] and analogues (1-(2-pyridylazo)-2-naphthol, (PAN))[20] have been proposed for the colorimetric determination of nickel. Nickel forms a pink-red complex with dimethylglyoxime (DMG) in a moderate alkaline solution, which can be quantified by gravimetry[22] or extracted for subsequent colorimetric determination.[21]

To detect trace amounts of metal in water samples, a chemical separation and preconcentration step is required before analysis. In this regard, different procedures such as solid-phase extraction (SPE),[23] liquid-phase extraction,[11,12] cloud point extraction,[18] and flotation[24] have been developed for the extraction and preconcentration of nickel in water matrices. Nickel-DMG complex ($Ni(DMG)_2$) is insoluble in water and can be extracted with organic solvents such as n-hexane,[24] and chloroform[25] or ionic liquid.[26] However, these chemical solvents may cause pollution for the environment as well as harm to health.

Currently, there is a growing interest in environmentally friendly and sustainable extraction methods that utilize greener solvents. In this regard, the last two decades have seen remarkable advancements in green solvents. Deep eutectic solvents (DESs) have emerged as a promising solvent class capable of replacing toxic organic solvents.[27] Some advantages of DES include low-cost, biodegradability, low toxicity and are easily prepared with highly variable viscosities.[28] However, early DESs were highly hydrophilic and unstable in aqueous solutions, hence resulting in a breakdown of the hydrogen bonds between their components.

Hydrophobic deep eutectic solvents (HDESs) were introduced in 2015 as a mixture of hydrogen-bound donors (long-chain length organic acids) with different hydrogen-bound acceptors (quaternary ammonium salts).[29] In these systems, the anion of the salt (*e.g.*, $Br^-$ of tetrabutylammonium bromide) serves as the hydrogen bond acceptor (HBA). Since then, HDESs have received much attention for broadening their applicability, including the removal of heavy metals from aqueous solutions.[30]

Smartphone-based digital image colorimetry (SDIC) is a novel, more accessible, and portable tool that enables quantitative analysis once limited to specialized laboratories with costly equipment.[31] Images captured with a smartphone camera are processed in different colour spaces (e.g., RGB, CMYK, CIELAB, and HSV) using software like Photometrix, Image J, Matlab, or Trigit, converting the colour data into analytical signals to establish a correlation between colour intensity and analyte concentration. Several studies have demonstrated the successful application of SDIC for monitoring metal concentrations in water.[11,32-34]

In this study, we introduce a method for preconcentration and determination of nickel in wastewater combining vortex-assisted liquid-liquid microextraction (VALLME) of the $Ni(DMG)_2$ complex with HDES composed of tetrabutylammonium bromide and decanoic acid (1:2) with smartphone-based DIC. An inexpensive image box equipped with a rechargeable, wireless illumination system was designed to capture images of the extraction tubes without the need to separate the HDES and aqueous phases. Colour space data were extracted from the digital images of the HDES phase using the free app Trigit,[37] with the magenta (M) channel of the CMYK model applied for nickel quantification.

## MATERIALS AND METHODS

### *Chemicals and solutions*

All chemicals were analytical grade and used as received without any further purification. Nickel chloride anhydrous (purity > 99%), DL-menthol (≥95%), thymol (98.5%) and ammonium chloride were purchased from Sigma Aldrich. Dimethylglyoxime, tetrabutylammonium bromide and ethanol absolute were purchased from Êxodo Científica (Sumaré, Brazil). Ammonium hydroxide, sodium phosphate monobasic monohydrate, sodium phosphate dibasic heptahydrate were purchased from Synth (São Paulo, Brazil). Octanoic acid and decanoic acid were purchased from Neon (São Paulo, Brazil). All solutions were prepared with ultra-purified water (electric resistivity of 18 Mohms cm) obtained from the Milli-Q system (Millipore).

A stock solution of nickel ions (1g $L^{-1}$) was prepared by dissolving anhydrous nickel chloride, dried in an oven at 100 °C for 2 hours and left in a desiccator overnight, in ultrapure water. Working solutions of Ni(II) were prepared by diluting the stock solution. Dimethylglyoxime (DMG) stock solution ($1.0 \times 10^{-2}$ mol $L^{-1}$) was prepared by dissolving 0.1161 g of the reagent in absolute ethanol. Working solutions of DMG were prepared by diluting the stock solution in the same solvent.

### *HDES synthesis*

To prepare HDESs, two components (HBA and HBD) were mixed at appropriate molar ratios, as previously reported.[35] HDES1 was prepared by mixing menthol and thymol in a 1:1 molar ratio. For HDES2 and HDES3, TBABr was combined with octanoic acid or decanoic acid, respectively, at a 1:2 molar ratio. HDES4 was prepared by mixing thymol and decanoic acid in a 1:1 molar ratio. Briefly, each component was weighed and mixed in a closed round-bottom flask, then mechanically stirred at 100 rpm and 65 °C until a homogeneous liquid was formed. The HDESs were stored at room temperature in the amber glass flasks sealed with parafilm.

### *Samples*

Nickel electroplating bath, rinse water, and wastewater samples were collected from the electroplating, washing, and effluent tanks, respectively, at a local electroplating industry. The rinse bath and wastewater were kept in a polypropylene bottle and stored at 4 °C until analysis. All samples were analyzed without pre-treatment.

### *Procedure*

For wastewater, the preconcentration step was performed directly in the samples without any pretreatment. However, due to the high nickel concentrations, the electroplating bath and rinse water samples were diluted with ultrapure water. The general procedure for VALLME and determination of nickel by SDIC is illustrated in Figure 1. Nickel samples and working solutions were determined by the following procedure: 10-mL aliquots of the Ni (II) solutions were transferred to glass tubes with screw caps, and pH was adjusted to 8.0 using a phosphate buffer solution. Then, 200 µL of 4.0 x $10^{-4}$ mol $L^{-1}$ dimethylglyoxime (DMG) were added, and the solution was mixed to ensure homogenization. After the formation of the pink $Ni(DMG)_2$ complex, 250 µL of the HDES were added, and the tube was vortexed for 60 seconds. After phase separation, the HDES phase was analyzed directly in the tube using smartphone-based DIC, eliminating the need to transfer it to another sample holder (*e.g.*, a cuvette). A blank sample was prepared following the same procedure, using ultrapure water instead of the nickel solution.

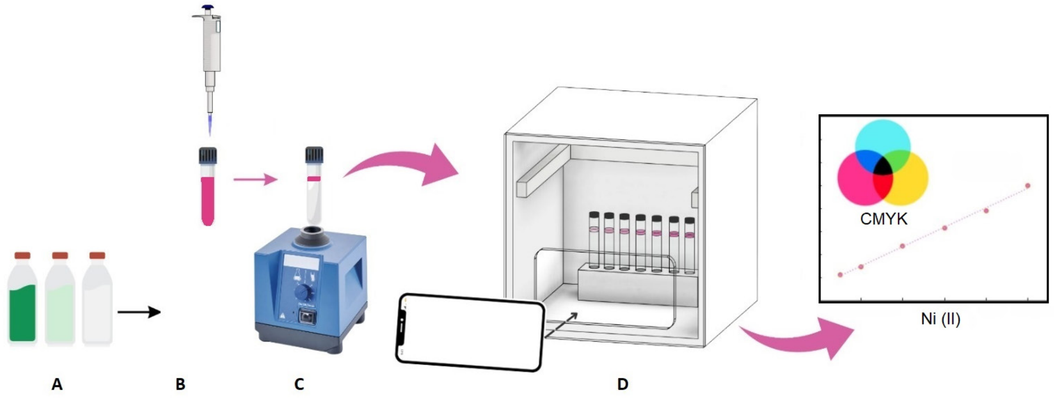

**Figure 1.** Schematic illustration of the procedure for nickel determination using SDIC: (A) Nickel samples (nickel bath, rinse water, and wastewater); (B) Ni-DMG complexation reaction; (C) VALLME with HDES; and (D) image capture.

To evaluate the greenness of the developed VALLME-DIC method for nickel determination, the Analytical Eco-Scale was employed.[36] This tool assigns penalty points (PPs) for factors such as toxicity, quantity of reagents, energy consumption, and waste, where a score ≥75 indicates excellent greenness.

### *Apparatus*

A custom image box (21 × 21 × 21 cm; height, width × length) was constructed from a cardboard box lined with white paper for optimal light reflection. A microextraction tube holder was made by drilling holes into a white expanded polyethylene (EPE) foam sheet (12 × 5 × 2.5 cm; length × width × height), designed to hold the glass tubes in an upright position during image capture. An observation aperture (14.8 × 7.2 cm) was created on the front of the box to accommodate the cell phone for capturing image samples. Wireless rechargeable LED lights with adjustable intensity controls and on/off switches were installed on the inner top and both sides of the box to ensure uniform illumination. The distance between the smartphone and the sample holder was kept constant at 15 cm throughout the experiments. Images were captured using an iPhone 15 (Apple), equipped with a 48 MP sensor camera, 26 mm focal length, $f$/1.6 aperture, and sensor-shift optical image stabilization. The digital images were saved in JPEG format and analyzed using the Trigit web app.[37] A rectangular region of interest (ROI) was defined with a selection tool, and colour data were automatically generated across multiple colour spaces (RGB, CMYK, HSV, and CIELAB). The analytical signal was calculated using the M channel values from the CMYK colour space for each sample and standard solution, subtracting the blank value within the same image.

## RESULTS AND DISCUSSION

### *Nickel-DMG reaction and studied parameters*

The aim of this work was to develop a cost-effective and greener microextraction procedure using HDES for the rapid determination of nickel in wastewater samples. To achieve this, a colorimetric method was developed using the traditional reagent dimethylglyoxime (DMG) in combination with vortex-assisted liquid-liquid microextraction (VALLME) and smartphone-based digital image colorimetry. The proposed procedure involves the complexation of Ni(II) ions by DMG in an alkaline buffered medium to produce the characteristic pink-red $Ni(DMG)_2$ complex according to the reaction: $Ni^{2+} + 2\ HDMG \rightarrow Ni(DMG)_2 + 2H^+$.

The $Ni(DMG)_2$ chelate is insoluble in water, forming the basis for gravimetric determination of Ni(II); however, it can be extracted into chloroform[21] or n-hexane[24] for subsequent colorimetric analysis. As an alternative to conventional volatile solvents, in this study four HDESs were evaluated for $Ni(DMG)_2$ extraction from aqueous solutions. These included two ionic, tetrabutylammonium-based HDES (TBABr:octanoic acid (1:2) and TBABr:decanoic acid (1:2)) and two nonionic, monoterpene-based HDES ((thymol-menthol (1:1) and thymol:decanoic acid (1:1)). Various extraction parameters were evaluated to optimize the VALLME of nickel-dimethylglyoximate, including the type and volume of HDES, pH of the nickel solution, DMG concentration, and vortex time. All experiments were conducted in triplicate using water samples spiked with nickel.

### *Image analysis*

The RGB colour space is the most common model used in digital image colorimetry. As expected, based on the colour of the $Ni(DMG)_2$ complex and complementary colours in the RGB model, a good correlation between analytical signal and nickel concentration was observed for the G (Green) channel, which corresponds to the complementary colour of the complex. However, pinkish-red colours in the RGB model lie midway between red and blue, which can lead to a less distinct signal. In contrast, the M (magenta) channel in the CMYK colour space closely corresponds with the colour of the $Ni(DMG)_2$ complex, resulting in improved sensitivity and linearity. Thus, the M channel was selected as the most effective for the analysis since it had the best correlation with nickel concentration.

### *HDES selection*

One of the most critical parameters affecting extraction efficiency is the extraction solvent. It is well-established that the extraction solvent should have some properties, such as lower density than water, low water miscibility, extraction capability of the target analyte, compatibility with the detection technique, and low toxicity.[38] HDESs can fulfil these requirements, making them quite useful as extraction solvents and a greener alternative to toxic volatile solvents. The obtained results confirmed the ability of HDESs for the extraction of $Ni(DMG)_2$ complex, with efficiency extraction values exceeding 90% (Figure 2).

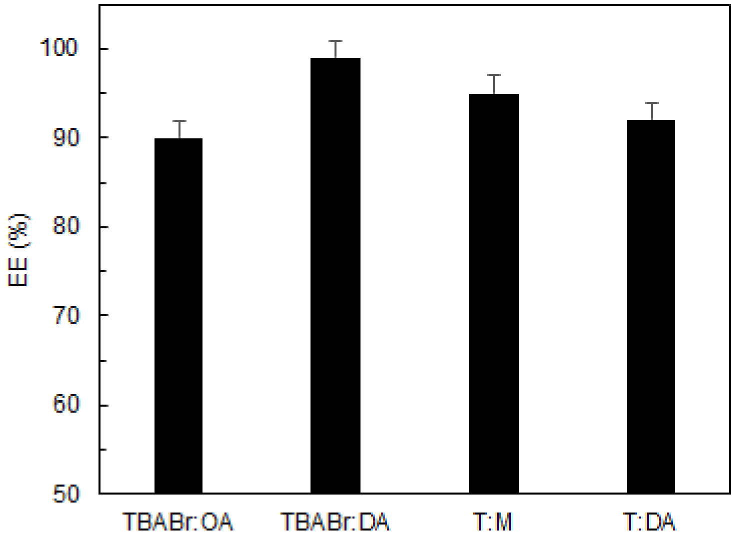

**Figure 2.** Effect of the type of HDES on the extraction efficiency. OA: octanoic acid, DA: decanoic acid, T: thymol, M: menthol. Experimental conditions: [$Ni^{2+}$] = 5 mg $L^{-1}$, sample volume = 5 mL, pH = 9, [DMG] = 1% (w/v) in ethanol, 200 µL, HDES volume = 500 µL, vortex time = 120 s.

Even HDESs present a capacity to absorb some amount of water that can influence the extraction of nonpolar analytes. The limited water solubility of $Ni(DMG)_2$ results from the formation of strong intramolecular O−H···O bonds within the dimethylglyoxime chelate.[39,40] Consequently, hydrogen bonds tightly hold the hydrogen, limiting the interaction of the O−H groups with water and inhibiting dissolution.

Therefore, the higher extraction efficiency observed with TBABr:decanoic acid over TBABr:octanoic acid may be attributed to the slightly higher polarity of octanoic acid (log $K_{ow}$ = 3.03) relative to decanoic acid (log $K_{ow}$ = 4.1). Probably, the lower water intake of TBABr:decanoic acid HDES contributes to maintaining a low-polarity environment that stabilizes the chromophore structure of the $Ni(DMG)_2$.

Furthermore, the HDESs composition affected the colour of the nickel-dimethylglyoximate. For both tetrabutylammonium-based HDESs the $Ni(DMG)_2$ complex formed exhibited its characteristic pink-red colour. In contrast, the non-ionic HDES thymol:menthol and thymol:decanoic acid presented distinct solvatochromic shifts, producing orange and pale-yellow complexes, respectively, which may be due to the nearly nonpolar environment.

Non-ionic HDES provided similarly high extraction efficiencies. However, the thymol:decanoic acid HDES exhibited emulsification and slow phase separation. Moreover, given that the weak colour of the complex in these nonionic HDESs could impact the sensitivity of colorimetric detection, TBABr:decanoic acid HDES was selected for further experiments.

### *Effect of pH*

Nickel-dimethylglyoximate formation and subsequent extraction are affected by the pH of the aqueous solution. Traditionally, the gravimetric determination and extraction of nickel-dimethylglyoximate from aqueous solution for colorimetric detection is achieved by adding a slight excess of ammonium hydroxide. The extraction of $Ni(DMG)_2$ by TBABr:decanoic acid HDES was investigated in the range of 5-10 (Figure 3). The results indicate that the extraction efficiency increased with pH, reaching a maximum at pH 7-9 before decreasing at pH 10, consistent with previously reported findings.[21,23]

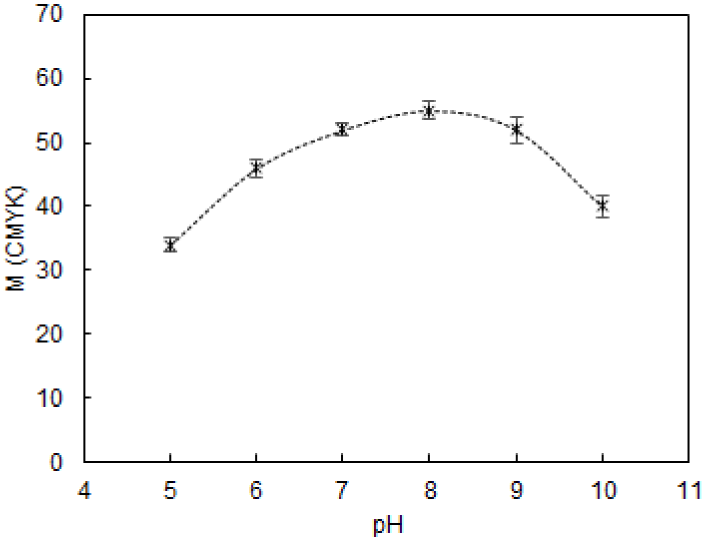

**Figure 3.** Effect of pH on analytical signal of Ni (II). Experimental conditions: [$Ni^{2+}$] = 5 mg $L^{-1}$, sample volume = 10 mL, [DMG] = 1% (w/v) in ethanol, 200 µL, HDES volume = 500 µL, vortex time = 120 s.

Remarkably, after vortexing, the HDES layer thickness at pH 8-10 remained consistent, in contrast to the noticeable thinning observed at pH levels 5 and 6. Studies have shown that the stability of HDESs when exposed to water depends heavily on the nature of both the HBA and HBD components.[41] If either the HBA or HBD component of an HDES is water-soluble, partial breakdown can occur, resulting in the hydrophilic component leaching into the aqueous phase.

Van Osch et al.[29] investigated the water stability of HDESs composed by ammonium salts and decanoic acid. The authors concluded that stability generally improves with longer alkyl chains in quaternary ammonium salts (HBAs), which lead to lower water content and reduced salt leaching. However, although the interfacial properties of HDESs with water have been explored,[42] the pH stability of HDESs in aqueous systems remains unexamined.

Our findings demonstrate the importance of pH to improve the stability of the HDES system. At basic solutions, the enhanced dissociation of decanoic acid ($pK_a$ 4.9) to its decanoate form at the oil-water interface could reduce hydrogen bonding interactions with the bromide anion, thereby promoting the leaching of the tetrabutylammonium cation ($TBA^+$) into the aqueous phase. In contrast, the presence of decanoate enhances electrostatic interactions with $TBA^+$, thereby supporting greater structural integrity of the HDES. Based on these observations, pH 8 was selected for further analytical procedures.

### *DMG concentration*

DMG is a well-known vicinal dioxime widely used as a chelating ligand for nickel, forming a complex with a 1:2 stoichiometric ratio (Ni(II):DMG). The effect of DMG concentration on the nickel extraction was examined in the range of $2 \times 10^{-5}$ to $8.0 \times 10^{-4}$ mol $L^{-1}$. The analytical signal increased with the addition of DMG up to $4.0 \times 10^{-4}$ mol $L^{-1}$, reaching a plateau and remaining constant (Figure 4). This result is supported by previous studies[24,26] in which nickel determination is conducted with an excess of DMG. Therefore, a DMG concentration of $4.0 \times 10^{-4}$ mol $L^{-1}$ was selected as the optimal concentration for $Ni(DMG)_2$ extraction.

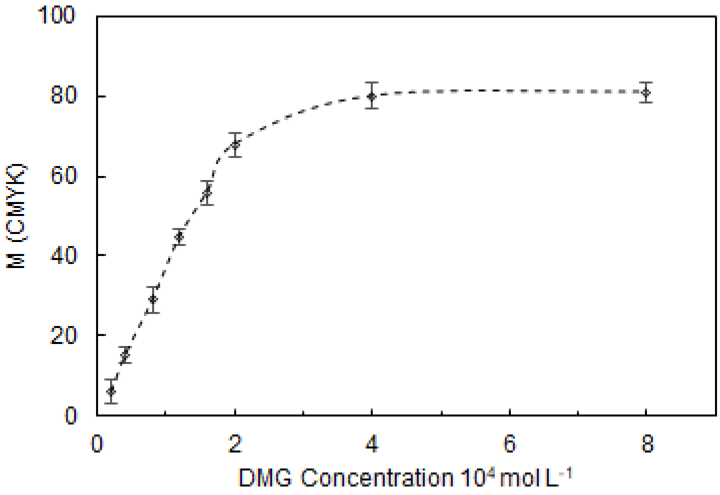

**Figure 4.** Effect of concentration of dimethylglyoxime (DMG). Experimental conditions: $[Ni^{2+}]$ = 5 mg $L^{-1,}$ sample volume = 10 mL, pH = 8, DMG = 200 µL, HDES volume = 500 µL, vortex time = 120 s.

### *Volume of HDES*

To evaluate the effect of extraction solvent volume, different volumes of the TBABr: decanoic acid HDES, ranging from 125 to 1000 µL, were tested. With increasing HDES volume, the extraction efficiency remained constant, but the analytical signal decreased, which can be attributed to the dilution effect of $Ni(DMG)_2$ in the larger solvent volume (Figure 5).

Although the 125 µL volume provided greater sensitivity, the HDES phase volume was not sufficient to fill the internal diameter of the tube and form a uniform layer on the surface of the aqueous phase for precise analysis by smartphone-based DIC. Consequently, 250 µL was selected as the optimal extraction HDES volume.

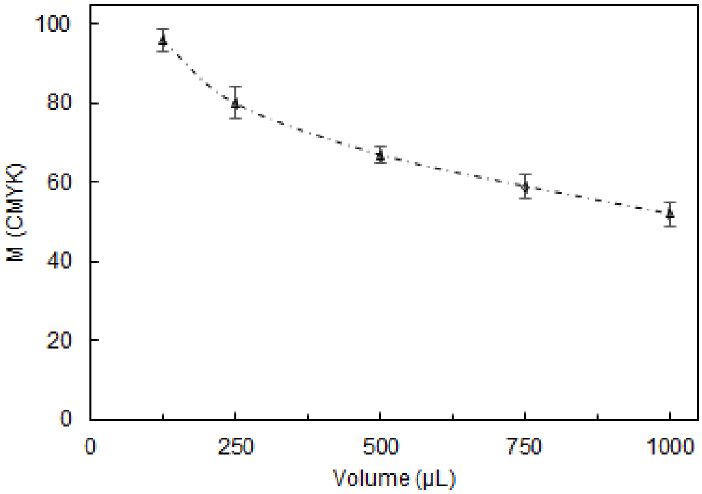

**Figure 5.** Effect of HDES volume on analytical signal. Experimental conditions: $[Ni^{2+}]$ = 5 mg $L^{-1}$, sample volume = 10 mL, pH = 8, DMG = 4.0 x $10^{-4}$ mol $L^{-1}$, 200 µL, vortex time = 120 s.

### *Vortex time*

Vortex-assisted liquid-liquid microextraction (VALLME) uses vortex mixing to disperse a microliter-sized droplet of extraction solvent in the aqueous samples.[43] This technique produces fine drops, which increase the interfacial area for mass transfer, decrease diffusion distance, and improve extraction efficiency. The effect of vortex time on extraction efficiency was evaluated over a range of 15 to 90 seconds at the maximum agitation speed (2,500 rpm). Figure 6 shows that the intensity of the analytical signal increased with vortex time up to 60 seconds over a range of 15 to 90 seconds at the maximum agitation speed (2,500 rpm). Therefore, 60 seconds was chosen as the optimal vortex time.

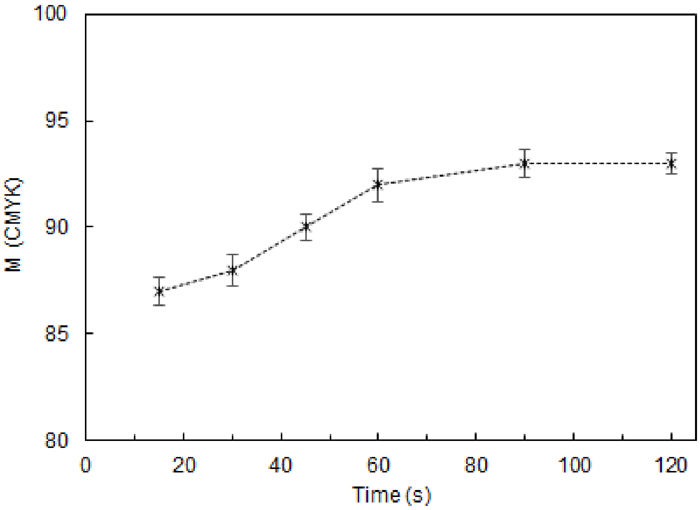

**Figure 6.** Effect of vortex time on analytical response. Experimental conditions: $[Ni^{2+}]$ = 5 mg $L^{-1}$, sample volume = 10 mL, pH = 8, DMG = $4.0 \times 10^{-4}$ mol $L^{-1}$, 200 µL, HDES volume = 250 µL.

### *Interferences*

Interference studies (Table I) were carried out using the proposed procedure to investigate the effects of $Cu^{2+}$, $Cr^{3+}$, $Fe^{3+}$, $Co^{2+}$, and $Fe^{2+}$, which also may be present in wastewater from the electroplating process. The determination of $Ni^{2+}$ (2 mg $L^{-1}$) in the presence of each metal cation at the 5 mg $mL^{-1}$ level demonstrated no interference from $Cr^{3+}$, $Fe^{3+}$, $Co^{2+}$, or $Fe^{2+}$. It is important to highlight those metals like iron ($Fe^{2+}$, $Fe^{3+}$), chromium ($Cr^{3+}$), and aluminum ($Al^{3+}$) can be removed from rinsewater by chemical precipitation through pH adjustment. Raising the pH with the addition of an alkali (*e.g.*, $Ca(OH)_2$, NaOH), these cations precipitate as hydroxides. Additionally, in the presence of oxygen, $Fe^{2+}$ oxidizes to ferric ion ($Fe^{3+}$), which precipitates as yellowish-orange ferric hydroxide at pH values above 3.5. Under experimental conditions, $Fe^{2+}$ and $Cu^{2+}$ affected the colour of the sample, although $Fe^{2+}$ did not impact the detection of nickel. $Cu^{2+}$ interfered with nickel determination, resulting in a decreased analytical signal, probably due to the formation of a thermodynamically stable chelating complex Cu-DMG. Copper interference became noticeable at concentrations approximately 1.5 times the level of nickel. However, there was no $Cu^{2+}$ in the samples analyzed.

To address the potential interference from $Cu^{2+}$ ions, which are commonly found in electroplating wastewater, additional experiments were conducted using a masking agent. As previously reported, a sodium thiosulfate masking solution was applied to eliminate the interference from $Cu^{2+}$ on determination of $Ni^{2+}$ by colorimetric analysis using 2-(2-thiazolylazo)-p-cresol.[44] The masking effect was observed after the addition of 1 mL of 0.25 mol $L^{-1}$ sodium thiosulfate, as evidenced by the relatively lack of significant decrease in the analytical signal upon the addition of copper ion. The addition of masking solution did not affect the signal of the $Ni(DMG)_2$ complex, confirming its suitability for improving method selectivity without compromising analytical performance.

**Table I.** Interference study of other metal ions on the nickel (2 mg $L^{-1}$) measurement by the proposed procedure

| Interfering Cation | Concentration (mg $L^{-1}$) | $Ni^{2+}$ Recovery (%) | Interference (%) |
|---|---|---|---|
| Control | 2 | 100 ± 2 | 0 |
| $Cr^{3+}$ | 5 | 100 ± 4 | 0 |
| $Fe^{3+}$ | 5 | 98 ± 3 | -2 |
| $Fe^{2+}$ | 5 | 102 ± 2 | +2 |
| $Co^{2+}$ | 5 | 99 ± 3 | -1 |
| $Cu^{2+}$ | 3 | 90 ± 4 | -10 |
| $Cu^{2+}$ | 5 | 64 ± 6 | -36 |
| *$Cu^{2+}$ | 5 | 97 ± 4 | -3 |

*after the addition of masking solution

### *Analytical features*

The analytical curve was linear in the concentration range of 0.45 to 5.9 mg $L^{-1}$. The regression equation was $y = 1.35 + 16.06x$ (where y is the M value and x is the nickel concentration), with a correlation coefficient of $R^2 = 0.9971$. The limit of detection (LOD) calculated as three times the standard deviation of the blank signal divided by the slope of the analytical curve was equal to 0.15 mg $L^{-1}$. The limit of quantification (LOQ), determined as ten times the standard deviation of the blank signal divided by the slope of the analytical curve, was 0.45 mg $L^{-1}$. Precision studies were conducted using spiked samples, with percentage coefficient of variation (% CV) values observed within assays at (2.6%) and between assays at (3.4%), indicating consistent repeatability and reproducibility.

### *Recovery*

To assess recovery (%), water samples were fortified with three known nickel concentrations and analyzed by the proposed method following the procedure described in the experimental section. Recoveries (%) were calculated as the measured amount divided by the spiked amount, multiplied by 100. The recovery rates (Table II) for the water samples were excellent, ranging from 97% to 104%.

**Table II.** Results of recovery obtained for nickel (mg $L^{-1}$) in water

| Sample | Spiked | Found | Recovery (%) |
|---|---|---|---|
| A | 0.50 | 0.52 ± 0.02 | 104 |
|  | 1.00 | 0.97 ± 0.04 | 97 |
|  | 2.00 | 2.04 ± 0.05 | 102 |
| B | 0.50 | 0.49 ± 0.01 | 98 |
|  | 1.00 | 1.03 ± 0.02 | 103 |
|  | 2.00 | 1.98 ± 0.03 | 99 |

### *Applications to real samples*

Nickel bath formulations typically combine nickel chloride, nickel sulphate, and boric acid. Rinsewaters is generated during the washing of plated items to remove residual plating solution and contaminants from metal electroplating operations and constitute a major portion of the waste. In general, in the electroplating industry, rinsewater is treated, and the final water can be then reused in the rinsing process or discharged. However, wastewater may still contain traces of heavy metals such as chromium, cadmium, copper, zinc, and nickel. The applicability of the proposed SDIC method following the VALLME procedure was evaluated through the analysis of nickel in nickel bath, rinsewater and wastewater samples of a galvanic industry (Table III).

**Table III.** Nickel amounts (mg $L^{-1}$) found in the samples by proposed method and comparative method (mean ± s)

| Samples | Proposed Method | PAN colorimetric Method | Relative Error (%) |
|---|---|---|---|
| Nickel bath* | 81 ± 1 | 79 ± 2 | +2.5 |
| Rinse water | 144 ± 3 | 142 ± 2 | +1.4 |
| Rinse water | 158 ± 3 | 159 ± 3 | -0.6 |
| Wastewater | 2.21 ± 0.02 | 2.30 ± 0.01 | -3.9 |
| Wastewater | 2.44 ± 0.01 | 2.37 ± 0.04 | +2.9 |

*g $L^{-1}$

To ensure readings remained within the linear range, the nickel bath sample was diluted 400,000-fold and the rinse water sample 100-fold. The results for the samples were compared with those from the 1-(2-pyridylazo)-2-naphthol (PAN) colorimetric method[20] for the measurement of Ni(II). Statistical analysis using a t-test indicated no significant difference between the methods at a 95% confidence level.

In this study, nickel levels in wastewater were slightly higher than the CONAMA-recommended limit (2 mg $L^{-1}$). However, this wastewater can be recycled back to the rinse baths.

### Comparison with other methods

For comparison purposes, the analytical features, including preconcentration technique, linear range, limit of detection (LOD), limit of quantification (LOQ), and sample volume of the proposed method and other extraction-based techniques coupled with FAAS, HPLC, and spectrophotometry, are compiled in Table IV.

**Table IV.** Comparison of analytical features of the proposed procedure and other published methods for the determination of nickel in water samples

| Technique | Extraction procedure | Linear range (mg $L^{-1}$) | LOD (mg $L^{-1}$) | LOQ (mg $L^{-1}$) | Sample volume (mL) | Ref. |
|---|---|---|---|---|---|---|
| FAAS | Cloud point LLME | 0.002-0.100 | 0.005 | 0.0016 | 50 | 11 |
| FAAS | LPME | 0.025-0.300 | 0.007 | 0.029 | 8 | 12 |
| HPLC | LLME | 0.001-0.010 | 0.008 | 0.001 | 5 | 13 |
| HPLC | SPME | 0.005-0.010 | 0.5 | --- | 10 | 14 |
| Spectrophotometry | Cloud point LLME | 0.2-5.0 | 0.10 | 0.20 | 10 | 18 |

(continued on next page)

**Table IV.** Comparison of analytical features of the proposed procedure and other published methods for the determination of nickel in water samples (continued)

| Technique | Extraction procedure | Linear range (mg L$^{-1}$) | LOD (mg L$^{-1}$) | LOQ (mg L$^{-1}$) | Sample volume (mL) | Ref. |
|---|---|---|---|---|---|---|
| Diffuse reflectance spectroscopy | SPME | 0.5-5.0 | 0.47 | 0.50 | 1 | 23 |
| Spectrophotometry | LLE | 0.60-12 | 0.10 | 0.60 | 50 | 24 |
| SDIC | VALLME | 0.45-5.9 | 0.15 | 0.45 | 10 | This work |

Both the FAAS[11,12] and HPLC[13,14] methods are highly sensitive, with a lower linear range and limit of detection; however, they require expensive laboratory equipment and volatile, flammable solvents, such as methanol or acetonitrile. In Table S1, the calculated penalty points (PPs) for the technique were 21 points (5 points for reagents and 16 points for instrumentation occupational hazard, energy consumption, and waste) revealing the excellent greenness (Eco-scale score 79) of the proposed VALLME procedure. Compared to other analytical methods (*e.g.*, cloud point extraction-FAAS, HPLC, spectrophotometry), our approach avoids the use of hazardous solvents like acetonitrile, methanol, and chloroform and reduces energy consumption and waste. Literature-reported methods for Ni determination have not been evaluated from this point of view, but the Eco-cale scores can be estimated between 50 and 70 due to higher solvent use, larger waste volumes, or non-portable instrumentation. Also, the cloud point LLME procedure is labour-intensive and time-consuming, allowing only 1-2 samples to be processed per hour. In addition to being inexpensive, the proposed smartphone-based method offers distinct advantages, with adequate sensitivity to monitor nickel levels in wastewater without requiring heating treatment, or dilution of the enriched phase, nor a skilled operator.

## CONCLUSIONS

In this study, VALLME of nickel-dimethylglyoxime complex with hydrophobic deep eutectic solvent for preconcentration and determination of Ni in water samples by smartphone-based DIC was presented and demonstrated for the first time. The significant advantage of the method is its simplicity because the image capture is performed directly in the extraction tube without the need to separate the extraction phase for subsequent analysis, unlike classical methods. The proposed procedure is fast, low-cost, eco-friendly, and demonstrates sufficient precision and accuracy for routine monitoring of nickel levels in electroplating industry wastewater.

### Conflicts of interest

The authors declare that there are no conflicts of interest.

### Acknowledgments

The authors thank grants #401681/2023-8 from CNPq, INCT Nanovida (CNPq/proc. 406079/2022-6) and 2024/04116-8 from FAPESP for the financial support granted during this research.

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## SUPPLEMENTARY MATERIAL

**Table S1.** Eco-Scale evaluation for the VALLME-SDIC procedure

| Reagents | Penalty Points (PPs) | | | Instruments/Others | PPs |
|---|---|---|---|---|---|
| | Amount PP | Hazard PP | Total PPs (Amount × Hazard) | | |
| Ethanol (<1 mL) | 1 | 4 | 4 | Vortex | 1 |
| Tetrabutylammonium bromide (TBABr, <0.1 g) | 1 | 6 | 6 | Image capture (Smartphone) | 0 |
| Decanoic acid (<0.2 g) | 1 | 2 | 2 | Occupational hazard | 0 |
| Sodium thiosulfate (1 mL, 0.25 mol $L^{-1}$) | 1 | 1 | 1 | Energy consumption (mild) | 1 |
| Phosphate buffer (1 mL, 0.1 mol $L^{-1}$) | 1 | 1 | 1 | Waste (12.3 mL/sample) | 3 |
| Dimethylglyoxime (DMG, 200 μL of $4\times10^{-4}$ mol $L^{-1}$) | 1 | 2 | 2 | | |
| **Subtotal PPs (reagents)** | | | **16** | **Subtotal instruments/others** | **5** |
| **Total PPs** | | | | | **21** |
| **Eco-Scale Score** | | | | | **79** |