Analytical Methods

ROYAL SOCIETY OF CHEMISTRY

PAPER

View Article Online
View Journal

Check for updates

Cite this: DOI: 10.1039/d5ay01045d

Ultrasound-assisted ionic liquid microextraction and colorimetric analysis for trace-level gold detection in environmental and geological samples

Fahad M. Alminderej,[a] Alaa M. Younis,[a] Alaa S. Amin *[b] and Hesham H. El-Feky[b]

A novel, precise, and targeted method has been developed for isolating, preconcentrating, and analyzing gold ions in water, ore, and food samples. This approach utilizes ultrasound-assisted dispersive liquid–liquid microextraction based on ionic liquids, combined with colorimetric detection of a distinct deep red hue. The compound 2-amino-4-(*m*-tolylazo)pyridine-3-ol (ATAP), introduced for the first time as a gold-specific chelating agent, was employed alongside the ionic liquid 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide in an ultrasonic bath maintained at 25 ± 2 °C for extraction. Following centrifugation, the gold complex was enriched within the ionic liquid droplets, and 200 μL of ethanol was added to the ionic liquid-rich layer prior to colorimetric analysis. Key variables influencing the recovery of Au^{3+} ions were systematically examined and fine-tuned to achieve optimal results. After fine-tuning both the instrumental and experimental conditions, the proposed method demonstrated a linear dynamic range for Au^{3+} ions between 4.0 and 240 ng mL^{-1}, with high molar absorptivity and a Sandell sensitivity of 1.22×10^6 L mol^{-1} cm^{-1} and 0.016 ng cm^{-2}, respectively. The method achieved quantification and detection limits of 3.92 and 1.30 ng mL^{-1}, respectively. A preconcentration factor of 500 was obtained. The relative standard deviation (RSD) was calculated to be 1.89% for gold ions at a concentration of 100 ng mL^{-1} ($n = 10$). No significant interference from various anions and cations was detected during the assessment of Au^{3+}. These findings confirm that the proposed technique is a fast, straight-forward, highly sensitive, selective, and effective analytical approach for isolating and quantifying Au^{3+} ions in environmental and geological samples, all while using minimal solvent volumes.

Received 22nd June 2025
Accepted 15th July 2025

DOI: 10.1039/d5ay01045d

rsc.li/methods

1 Introduction

In natural samples, the content of noble metals is typically at ultra-trace levels and their assessment needs preconcentration from matrix elements. Gold possesses specific features that contribute to its widespread industrial applications.[1] Gold, renowned for its extensive applications in areas such as jewelry, stands as one of the most indispensable and valuable precious metals. Consequently, several techniques for assessing gold in mineral and wastewater have been applied.[1–3] The concentration of gold is approximately 4.0 ng g^{-1} in basic rocks and 1.0 ng g^{-1} in soils. In aquatic environments, gold levels are reported to be around 0.2 ng mL^{-1} in river water and 0.05 ng mL^{-1} in seawater.[4] The presence of gold in geological and environmental samples is usually at extremely low concentrations, rendering direct measurement through atomic absorption spectrometry (AAS) ineffective due to inadequate sensitivity and interference from sample matrices. Consequently, isolating and concentrating the analyte are crucial for reliable gold analysis.[5]

Various procedures have been developed to separate and preconcentrate gold, such as coprecipitation,[6] sorbent extraction,[7] liquid–liquid extraction (LLE),[8] dispersive liquid–liquid microextraction (DLLME),[9] cloud point extraction (CPE),[10] solid phase extraction (SPE),[11] dispersive micro-solid phase extraction (NM-d-μSPE)[12] and electro-deposition.[13] In industrial gold extraction, cyanide is commonly used as a leaching agent.[2,3] Gold recovery through the adsorption of auro-cyanide complexes on activated carbon is a well-demonstrated process.[14] Nevertheless, there is high interest in the non-cyanide procedure application for gold dissolution due to the inability and toxicity of cyanide to effectively leach complex ores.

Numerous advanced techniques have been employed for gold detection, such as fluorometry,[15] X-ray fluorescence,[16] ranelate-induced nanoparticle formation,[17] paper-based sensors,[18] optical films,[19] and capillary electrophoresis.[20] However, these methods often involve complex workflows, high-cost instrumentation, and substantial use of toxic organic solvents, which restrict their broader applicability. Various

---

[a] Department of Chemistry, College of Science, Qassim University, Buraidah, 51452, Saudi Arabia

[b] Chemistry Department, Faculty of Science, Benha University, Benha, Egypt. E-mail: asamin2005@hotmail.com

atomic spectroscopic techniques (from graphite furnace AAS to ICP-OES and ICP-MS) have been widely used for trace analysis of gold[21–24] and allow for detection at very low concentrations. However, these methods are relatively expensive and difficult to apply. While these techniques offer a minimal limit of detection, they can be time-intensive, financially burdensome, and susceptible to interference from the sample matrix.

Solid-phase extraction (SPE) has gained significant popularity over traditional liquid–liquid extraction (LLE) due to its numerous advantages, including cost-effectiveness, high analyte recovery, improved enrichment capability, faster phase separation, minimal use of organic solvents, and compatibility with various detection techniques in both online and offline modes.[25] Several materials, like carbon nano-tubes (CNTs),[26] ion-imprinted thiocyanato-functionalized mesoporous silica,[27] C18 silica gel membrane disks,[28] and Amberlite XAD-2000 resin,[29] have proven effective as sorbents to separate and preconcentrate ultratrace levels of Au ions.

Diverse sample preparation systems have been described for gold ion separation from several matrices before its assessment, like cloud point CPE,[30] coprecipitation,[31] SPE,[10] and LLE.[32] Traditional LLE is the greatest and most effective procedure to extract a series of organic and inorganic components in analytical chemistry. Unfortunately, it consumes time and large volumes of toxic organic solvents.[33] The extraction techniques developments gained great attention for its miniaturization from the analytes, lately, cheapness, effectiveness, simplicity, and minimized reagent consumption. Dispersive liquid–liquid microextraction (DLLME) was studied and established by Assadi and his co-workers. It is more powerful and highly efficient at preconcentrating and assessing inorganic and organic ultra-trace species in water samples.[34] Simplicity, ease of operation, low organic solvent cost, low sample volume, high recovery, and high enhancement parameters are several of the outstanding advantages of DLLME. This microextraction method was used to assess trace amounts of gold ions in various types of environmental samples.[35]

Ionic liquids (ILs) are novel green chemicals that have gained recognition in both the chemical industry and academia. This innovative class of chemicals offers the potential to reduce the reliance on harmful organic solvents due to their distinctive properties. Their minimal volatility is a key feature that defines them as environmentally friendly, sustainable solvents.[36–38] Utilizing both ultrasonic bath and probe systems, ultrasound-assisted extraction has emerged as a highly effective technique for ultra-trace analysis, facilitating the extraction of trace metals from a wide range of sample matrices during the preparation process.[39,40] Traditional extraction methods typically demand substantial quantities of high-purity solvents, which can pose environmental and safety risks due to their tendency to volatilize.[41] To address these concerns, various microextraction approaches, such as cloud point extraction, have been developed and reported.[42,43]

The novelty of this study lies in exploring a sustainable approach for isolating and enriching gold(III) ions. To the best of our knowledge, this is the first time ATAP has been used for Au^{3+} ion complexation. The investigation centers on a technique combining ultrasound-enhanced dispersive liquid–liquid microextraction (USA-DLLME) with spectrophotometric measurement, providing a comprehensive evaluation of its practical application. The process involves complexing gold(III) ions with 2-amino-4-(*m*-tolylazo)pyridine-3-ol (ATAP), a novel reagent used to facilitate the extraction and preconcentration of Au^{3+} ions. This is accomplished *via* an ionic liquid-based ultrasound-assisted dispersive liquid–liquid microextraction (IL-USA-DLLME) procedure, subsequently analyzed through colorimetry. IL-USA-DLLME utilizes ultrasound to expedite or induce the movement of material between distinct phases.[44]

Colorimetric methods are widely used in trace analysis due to their affordability and ease of use. However, traditional colorimetric techniques often lack the sensitivity needed to directly measure gold ions in geological samples at the μg L^{-1} level.[45–48] The main goal of the present method is to achieve accurate measurements at these low concentrations; a preconcentration step is typically required.

2 Materials and methods

2.1. Instrumentation

The ionic liquid, 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide [Omim] (Sigma-Aldrich), underwent uniform mixing using Sonorex ultrasonic baths (manufactured by Bandelin, Germany) operating at a frequency of 35 kHz for a duration of 2.0 minutes. A thermostatic water bath (Low Speed Centrifuge, CFG-550JP with a maximum speed of 6000 rpm), ensuring precise temperature regulation, and a centrifuge utilizing 25 mL graduated centrifuge tubes (supplied by Superior, Germany) were employed to expedite the separation of phases. Measurements were conducted using a PerkinElmer Analyst 100 atomic absorption spectrometer (originating from the USA). Absorbance spectra were documented with a PerkinElmer Lambda 12 UV/Vis spectrometer (supplied by PerkinElmer, USA), utilizing a 1.0 mm quartz cuvette. Solution pH values were verified with an Orion Research model 601 A Digital Ionalyzer pH meter (supplied by Orion, Japan).

2.2. Sample solutions and reagents

A stock standard solution of gold at a concentration of 1000 μg mL^{-1} was obtained from Merck (located in Darmstadt, Germany). Lower concentration working solutions were created through appropriate dilution of this stock solution using double-distilled water. The synthesis of [Omim] followed established procedures.[49–51] The surfactants Triton X-100 and Triton X-114 were procured from Fluka (situated in Busch, Switzerland). Prior to utilization, 25 mL conical bottom centrifuge tubes underwent a cleaning process involving immersion in a 10% nitric acid solution for a minimum of 24 hours, followed by thorough rinsing with double-distilled water.

The compound 2-amino-4-(*m*-tolylazo)pyridine-3-ol (ATAP), utilized in this study, was synthesized following a previously reported method.[52] A suitable quantity of the substance was dissolved in 100 mL of ethanol procured from Fluka (situated in

Busch, Switzerland) to create a 3×10^{-3} M solution. This prepared solution maintained its stability for a period exceeding two weeks. Buffer solutions spanning a pH range of 2.75 to 11.63, encompassing borate, acetate, thiel, phosphate, and universal buffers, were formulated using acetate, borate, and phosphate salts with their acids and NaOH procured from Fluka (situated in Busch, Switzerland) according to established protocols.[53]

2.3. Extraction protocol

A 20 mL aliquot of the sample and reference solutions, containing gold ions (Au^{3+}) at concentrations between 0.1 and 6.00 μg mL^{-1}, along with 1.5 mL of ATAP (3×10^{-3} M), underwent pH adjustment to 6.5. This was accomplished by introducing 3.0 mL of universal buffer solution within a 25 mL conical centrifuge tube made of glass. The mixture was then subjected to a temperature of 90 °C for 10 minutes to induce the creation of the gold–ATAP compound. This complex formation is crucial for liquid-phase microextraction (LPME) of elements, aiding the transfer of the Au^{3+} complex into the organic solvent.[54] The ATAP reagent served a twofold purpose. Initially, it bound to the Au^{3+} ions, thus enhancing the LPME process and making the extraction more efficient. By forming these complexes, ATAP enabled the selective removal of gold. Subsequently, 2.0 mL of Triton X-100 (at a concentration of 0.1% v/v), 0.5 mL of sodium nitrate (2.0%, w/v), and 75 mg of [Omim][TF_2N] were incorporated into the mixture. The tube was then placed in an ultrasonic bath until the solution became turbid. This turbidity resulted from the dispersion of minute [Omim][TF_2N] droplets within the aqueous sample by the ultrasonic treatment, a process that took approximately 2.0 minutes. The Au^{3+} complex was thus extracted into these tiny [Omim][TF_2N] droplets. The resulting blend was then centrifuged at 4000 rpm for 3.0 minutes. This centrifugation caused the dispersed [Omim][TF_2N] droplets to settle at the bottom of the conical tube. The majority of the aqueous layer was then carefully poured off (decanted). The ionic liquid (IL) phase was then dissolved in 200 μL of 95% ethanol. The final solution was transferred to a quartz cuvette with a 1.0 mm path length, the absorption spectrum against a reference was recorded over the wavelength range of 350–700 nm and its light absorption was measured at the wavelength of maximum absorbance (λ_{max} 587 nm). A control sample, prepared in the same manner but without the addition of Au^{3+} ions, was used as a blank.

2.4. Sampling

2.4.1. Collection and preparation of water specimens for gold analysis.[55] Four distinct water sources were sampled: a stream (Shoubra, Egypt), the Nile River (Benha, Egypt), seawater (Alexandria, Egypt), and Zamzam well water (Saudi Arabia). Upon collection, these samples were treated with 0.2 M nitric acid (HNO_3) to stabilize them and then passed through a cellulose nitrate filter with a pore size of 0.2 μm to remove larger particles. To validate the analytical method, the gold concentration in the water samples was determined using the previously detailed procedure. Additionally, known quantities of standardized gold solutions (50, 100, and 150 ng mL^{-1}) were added to separate portions of each water sample to create spiked samples. These spiked samples were allowed to equilibrate overnight. The resulting gold concentration in these enhanced samples was then measured. Prior to analysis, all water specimens underwent filtration using a Millipore cellulose membrane filter with a pore size of 0.45 μm to eliminate any remaining particulate material. The pH of these filtered samples was adjusted to approximately 6.5, after which the previously outlined extraction protocol was implemented.

2.4.2. Gold content analysis in ore samples. A 1.00 g portion of ore was placed in a ceramic container and subjected to high-temperature oxidation in a furnace at 650 °C for a duration of 2.0 hours.[56] Following this heating process, the treated sample was transferred to a 250 mL vessel, where it was combined with 50 mL of freshly prepared acid mixture (*aqua regia*). To maintain the stability of the gold chloride compound during subsequent heating, 0.5 g of sodium chloride (NaCl) was incorporated. The vessel was covered and heated on a hot plate for 4.0 hours, with periodic additions of more acid mixture to ensure sufficient acidic conditions. The cover was then removed, and the liquid volume was carefully reduced through evaporation until near dryness. Subsequently, 40 mL of a concentrated hydrochloric acid solution (6.0 M) was added, and the mixture was gently heated until a clear solution was obtained. After cooling, the solution was passed through a filter paper with an 11 μm pore size (Whatman No. 1) to remove any solid particles. The remaining solid material was rinsed with a small amount of dilute hydrochloric acid (0.1 M). The filtered liquid was then carefully transferred to a 100 mL volumetric flask, and the gold concentration was determined using the previously described extraction method after adjusting the pH to approximately 6.5.

2.4.3. Creation of standardized reference material samples. To validate the developed gold extraction and analysis method,[57] three geochemical reference materials (GAUs 15, 16, and 17) were processed. For each GAU, a precise 0.50 g portion was weighed and dissolved using *aqua regia*. The resulting mixture was heated until all liquid evaporated, ensuring the complete removal of nitrogen oxides. A small quantity of concentrated hydrochloric acid (HCl) was then added, followed by 15 mL of purified water (double-distilled). This mixture was then filtered to remove any insoluble residues. The entire filtered solution was carefully transferred to a 25 mL volumetric flask. Finally, the flask was filled to the calibration mark with additional purified water to achieve the desired final volume. The gold concentration in these prepared solutions was then adjusted to pH 6.5 and measured using the previously described analytical procedure.

2.4.4. Processing of actual food matrices. Crustaceans and fish were acquired from four different retail food stores situated at random locations in proximity to the Suez Canal, Egypt. Following procurement, four specimens of each were immediately placed in chilled containers with ice and transported to the laboratory, where they were stored at −20 °C until processing.[58] This collection occurred in January 2025. The edible muscle portions of the seafood were subjected to lyophilization (freezedrying) until a stable mass was attained and then pulverized into a fine powder. Roughly 0.5 g of the pulverized material was then subjected to chemical breakdown using 5.0 mL of concentrated nitric acid (HNO_3) at 135 °C for a period of 4.0 hours. Subsequently, 1.0 mL of a 30% hydrogen peroxide (H_2O_2) solution and 1.0 mL of concentrated perchloric acid ($HClO_4$) were introduced. The temperature was elevated to and maintained at 150 °C until the resulting liquid became transparent and any remaining solid matter transformed into a white or gray residue. After filtration, the clear liquid was diluted to a final volume of 250 mL. The acidity/alkalinity of the diluted solution was then adjusted to a pH of 6.5 in preparation for subsequent analysis. The determination of gold concentration was performed using the previously described analytical protocol.

2.4.5. Soil specimen processing. Soil was gathered from agricultural land near a gold fabrication facility in Abou-Tartour, Egypt. A 50 mg mass of this soil was precisely measured and combined with 20 mL of concentrated hydrochloric acid (HCl), followed by agitation at 50 °C. After a 4 hour settling period, the mixture underwent centrifugal separation at 2500 rpm.[59] The supernatant (clear liquid) was then adjusted to a pH of 6.5 and transferred to a 250 mL graduated flask. Deionized water with buffer solution of pH 6.5 was added to bring the solution to the specified volume for subsequent analysis. The quantification of gold within the prepared solution was executed using the previously detailed analytical methodology.

3 Results and discussion

To achieve maximum recovery of Au^{3+} ions, the ideal experimental parameters for extraction needed to be determined. This involved examining the impact of several variables, including the concentration of sodium nitrate ($NaNO_3$), the concentration of ATAP in ionic liquid-assisted ultrasound-dispersive liquid–liquid microextraction (IL-USA-DLLME), the pH of the solution, the amount of ionic liquid used, and the duration of both centrifugation and sonication. Within the context of the IL-USA-DLLME/spectral analysis method, the extraction efficiency (percentage of extraction) and the enhancement factor were calculated using the following equations:

$$\text{Percentage of extraction} = C_{\text{org}}V_{\text{org}}/C_{\text{aq}}V_{\text{aq}} \times 100 \qquad (1)$$

$$\text{Enhancement factor} = C_{\text{org}}/C_{\text{aq}} \qquad (2)$$

In these calculations, V and C denote volume and concentration, respectively. The subscripts "org" and "aq" signify the organic and aqueous phases, respectively. The concentration in the organic phase (C_{org}) was determined using a calibration curve generated from standard solutions of Au^{3+} prepared in ethanol.

3.1. Ionic liquid screening

The distinctive characteristics of ionic liquids (ILs) are primarily determined by the capacity of their constituent salt to function as both a supplier and a receiver of hydrogen bonds, along with the degree to which electrical charges are localized on the anionic component.[38,60] The inherent ability to form hydrogen bonds, the distribution of charge across the anions, the overall polarity, and the extent of dispersive forces are fundamental elements that influence the observable properties of ILs.[61] Ionic liquids based on the imidazolium cation exhibit a high degree of hydrogen bonding organization and exert a considerable influence on chemical reactions and various processes. The formation of two-phase systems is often facilitated by ILs containing the [TF_2N] anion, primarily due to their lack of miscibility with aqueous solutions. The environmentally benign nature often attributed to ILs is typically associated with their exceptionally low volatility.[35,62] Although ILs do not readily vaporize and therefore do not directly contribute to atmospheric contamination, this does not inherently imply that they pose no environmental risk. The [TF_2N] anion demonstrates the optimum due to enhanced stability in the presence of water and offers additional benefits owing to its hydrophobic nature.

3.2. Effect of ionic liquid amount

Stock solutions of [Omim][TF_2N] with a concentration of 25 mg L^{-1} were created using propanone. The quantity of the [Omim][TF_2N] ionic liquid employed is a key determinant in obtaining substantial analyte extraction. However, excessive amounts of this liquid can lead to an unfavorable phase volume ratio. Therefore, the experimental setup was designed to determine the minimum quantity of the IL phase needed to maximize the preconcentration factor. The impact of varying IL amounts (ranging from 15 to 150 mg added to a 25 mL sample) on extraction recovery was investigated. The results indicated a strong correlation between the IL quantity and the performance of the extraction method. As represented in (Fig. 1), optimal extraction was achieved with 75 mg of the ionic liquid,

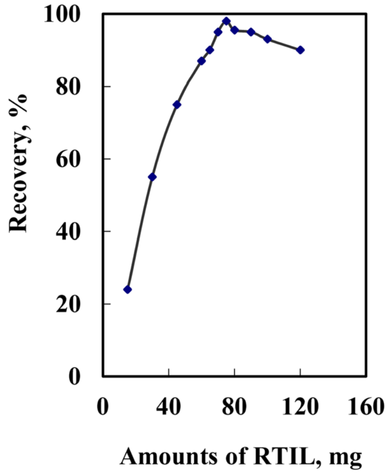

Fig. 1 Effect of amount of RTIL on the recovery of gold. Utilized conditions: Au^{3+} 100 ng mL^{-1}, pH 6.5, ATAP 1.8 × 10^{-4} M, $NaNO_3$ 0.04% (w/v), Triton X-100 0.002% (w/v), and diluting agent 200 µL ethanol.

with no appreciable improvement observed at higher quantities. Considering the need for effective enrichment, low resistance to flow, and a pronounced aversion to water, a quantity of 75 mg of the IL was chosen as the most suitable amount for the extraction process.

3.3. Influence of acidity and alkalinity

The level of acidity or alkalinity (pH) of the sample solution plays a crucial role in the IL-USA-DLLME method, as it directly influences both the formation of a complex with adequate water repellency and the subsequent extraction process. The impact of pH on complex formation was examined across a range from 2.75 to 11.66, while keeping all other experimental conditions unchanged. At pH values below 3.5, the nitrogen atoms of ATAP become positively charged (protonated), restricting the available binding sites for Au^{3+} ions. Conversely, within a pH range of 6.0 to 7.0, the hydroxyl group of ATAP loses a proton (deprotonated), allowing Au^{3+} to bind with the azo nitrogen, resulting in successful complex formation. Under alkaline conditions, the conversion of Au^{3+} to $Au(OH)_3$ leads to a reduction in the effectiveness of Au^{3+} separation and concentration. The experimental data (Fig. 2) indicate that consistent extraction is observed within the pH range of 6.0 to 7.0. Therefore, a pH value of 6.5 was determined to be optimal for all subsequent analyses.

3.4. Impact of ATAP concentration

The effect of ATAP concentration on the extraction efficiency of Au^{3+} ions using the IL-USA-DLLME technique was investigated across a range of 0.2–3.0 × 10^{-4} M. The experimental findings (illustrated in Fig. 3) demonstrated that the light absorption of the formed complex increased proportionally with ATAP concentration up to a value of 1.6 × 10^{-4} M, beyond which no further increase in absorption was observed. Consequently, an ATAP concentration of 1.8 × 10^{-4} M was selected for subsequent experiments.

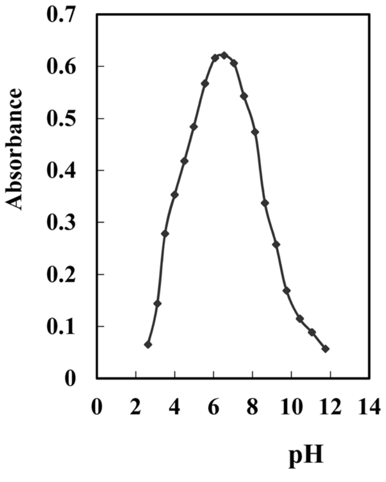

Fig. 2 Effect of pH on the recovery of 100 ng per mL Au^{3+}. Conditions are the same as in Fig. 1 except for pH.

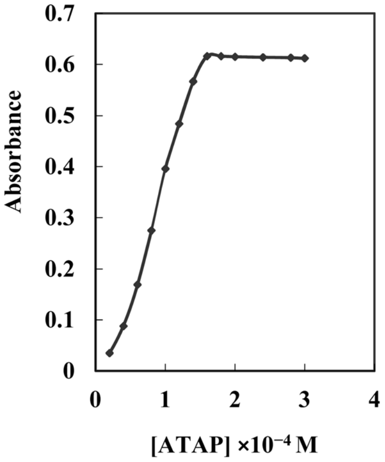

Fig. 3 Effect of ATAP concentration on the recovery of 100 ng per mL Au^{3+} ions. Conditions are the same as in Fig. 1 except for the concentration of ATAP.

3.5. Influence of salinity

Elevating the salt concentration has been previously suggested for single-drop microextraction (SDME),[62,63] dispersive liquid–liquid microextraction (DLLME),[64] and hollow-fiber liquid-phase microextraction (HF-LPME).[65,66] The volume of the extraction phase can be altered by the presence of salts through either a "salting-in" or a "salting-out" phenomenon.[67] However, a notable property of ionic liquids (ILs) is that the solubility of [Omim][TF_2N] remains largely unaffected even in solutions with high salt concentrations. Furthermore, due to their high density, the minute droplets of the extraction phase readily separate in saturated salt solutions,[68,69] thus preventing the target analytes from adhering to the container walls. Additionally, because of the extremely limited solubility of water-repelling ILs in aqueous solutions, the influence of residual salt from the sample matrix is minimal.[67] Consequently, it is anticipated that increasing the salt concentration will not significantly alter the volume of the extraction phase. Sodium nitrate ($NaNO_3$) was employed to assess the impact of salinity within a concentration range of 0.0–1.0% (w/v). A minor enhancement in Au^{3+} recovery was observed up to a $NaNO_3$ concentration of 0.04% (w/v), likely due to a salting-out effect. However, no further changes in recovery were noted between 0.05% and 1.0% (w/v). Therefore, the IL-USA-DLLME technique can be effectively used to isolate and concentrate Au^{3+} ions from samples containing up to 2.0% (w/v) salt. A $NaNO_3$ concentration of 0.04% (w/v) was chosen for all subsequent experiments to maximize recovery.

3.6. Selection and quantity of anti-sticking agent

After centrifugal separation, we observed that a portion of the ionic liquid (IL) phase adhered to the centrifuge tube walls. To mitigate this issue, non-ionic surface-active agents were introduced into the samples.[70] These surfactant molecules, through the process of phase separation, formed a coating around the minute IL droplets. This encapsulation reduced the interaction between the IL and the tube walls, effectively preventing the IL phase from sticking. Two distinct non-ionic surfactants, Triton X-100 and Triton X-114, were evaluated and their effects contrasted. While the use of Triton X-114 resulted in a reduction in recovery, the inclusion of Triton X-100 led to an improvement. Therefore, Triton X-100 was selected as the preferred anti-adhesion additive. A concentration of 0.008% (w/v) was determined to be the optimal concentration for use within the IL-USA-DLLME methodology. Although Triton X-100 reduces IL adhesion, it is an environmentally concerning surfactant. Its use does not contradict the "green" claims and eco-friendlier alternatives.

3.7. Influence of ultrasonic treatment duration

The rate of analyte movement from the aqueous phase is hindered by the viscosity of the extraction solvent. In the IL-USA-DLLME method, creating a turbid mixture significantly enhances the contact surface between the extraction solvent and the main aqueous sample.[49] Therefore, effective dispersion is essential for successful extraction. The duration of ultrasonic treatment is a critical parameter in this process. Extending the sonication period promotes greater dispersal of the extracting solvent within the aqueous solution, leading to more pronounced turbidity. The impact of sonication time was investigated over a period of 1.0 to 5.0 minutes. It was observed that a minimum of 2.0 minutes of sonication was necessary to achieve complete turbidity. Consequently, a duration of 2.0 minutes was selected as the optimal time for the dispersion step.

3.8. Influence of the centrifugal separation duration

The duration of centrifugal separation is a key factor influencing the isolation of the ionic liquid from the aqueous phase. An investigation was conducted using centrifugation times ranging from 1.0 to 7.0 minutes at a rotational speed of 4000 rpm. Extended centrifugation periods can cause the ionic liquid to redisperse within the aqueous phase, while insufficient centrifugation time hinders proper phase separation. Consequently, a centrifugation duration of 3.0 minutes was determined to be the most effective.

3.9. Nature of the fixed complex

The stable Au^{3+}–ATAP complex was investigated at pH 6.5 employing Job's continuous variation and molar ratio approaches. By altering the concentration of ATAP, the graph of A against the [ATAP]/[Au^{3+}] molar ratio exhibited a distinct inflection point at a 1 : 1 ratio, suggesting the formation of a stable complex containing one ATAP molecule. Furthermore, the Job's process demonstrates a ratio [ATAP]/[Au^{3+}] of 1.0. As a result, the findings confirmed a stoichiometric proportion of 1 : 1 between [ATAP] and [Au^{3+}], consistent with values observed in aqueous solution. ATAP can function as a bidentate ligand, featuring two donor atoms positioned within the same plane. The metal ion forms coordination bonds with both the azo-linked nitrogen and the hydroxyl group adjacent to the aromatic ring in the ATAP structure.

3.10. Effect of the coexisting ion

The selectivity of the IL-USA-DLLME method for gold isolation was evaluated by examining the impact of commonly encountered ions present in both water and ore matrices under optimized conditions. The tolerance threshold was defined as the highest concentration of interfering ions that resulted in a measurement error of no more than 5.0% in the sample's light absorption. The obtained data revealed that the presence of substantial quantities of cations and anions typically found in real samples did not exert a significant influence on the IL-USA-DLLME method when used for gold determination. Although ATAP reacts with copper ions using CPE under variable conditions, it does not indicate any interference under the optimum conditions used in the present work. Furthermore, the majority of transition metals, including palladium and platinum, exhibited no interference with tolerance limits of 200- and 100-fold excess of Au^{3+} ions, respectively, indicating acceptable selectivity for gold extraction (Table 1). Selectivity was validated in real complex matrices (*e.g.*, ore/soil with high metal loads) beyond spike recovery.

3.11. Analytical performance

The performance of the IL-USA-DLLME method was evaluated by determining various analytical characteristics, including quantitation capabilities, repeatability, detection limit, correlation coefficient, linear dynamic range, enrichment factor, calibration function, and precision (Table 2).

The calibration function was generated by subjecting a series of standard solutions to the IL-USA-DLLME procedure, followed by spectrophotometric measurement. Linearity was observed for Au^{3+} concentrations ranging from 4.0 to 240 ng mL^{-1} in a 25 mL sample. The linear relationship between absorbance (A) and Au^{3+} concentration (C, expressed in μg L^{-1} in the final solution) was described by the equation $A = 6.21C + 0.007$, with a correlation coefficient of 0.9988. For more accurate analysis, the Ringbom optimum concentration range was evaluated by

Table 1 Effect of foreign ions on the recovery of 100 ng per mL Au^{3+} ions

Ion	Added	As concentration (μg L^{-1})	Recovery (%)
K^+	KCl	25 000	101.5 ± 2.5
Na^+	$NaNO_3$	20 000	101.5 ± 3.0
$SO_4{}^{2-}$	Na_2SO_4	15 000	97.7 ± 1.5
$PO_4{}^{3-}$	KH_2PO_4	10 000	98.2 ± 2.0
Ca^{2+}	$Ca(NO_3)_2\cdot 4H_2O$	7500	102.8 ± 2.5
Mg^{2+}	$Mg(NO_3)_2\cdot 6H_2O$	6000	98.5 ± 3.0
Cu^{2+}	$Cu(NO_3)_2\cdot 3H_2O$	4500	97.4 ± 1.0
Zn^{2+}	$Zn(NO_3)_2\cdot 6H_2O$	3000	102.5 ± 2.0
Fe^{3+}	$Fe(NO_3)_3\cdot 9H_2O$	1750	102.6 ± 2.5
Mn^{2+}	$Mn(NO_3)_2\cdot 4H_2O$	1000	99.6 ± 4.5
Ni^{2+}	$Ni(NO_3)_2\cdot 6H_2O$	600	99.3 ± 3.8
Pb^{2+}	$Pb(NO_3)_2$	200	100.4 ± 3.5
Pd^{2+}	$Pd(NO_3)_2$	20	97.5 ± 2.5
Pt^{4+}	H_2PtCl_6	10	103.5 ± 3.5

Table 2 Analytical features of the proposed method

Parameters	IL-USA-DLLME	Before IL-USA-DLLME
Amount of ethanol	200 μL	10 mL
pH	6.5	6.5
Optimum [ATAP]	1.8×10^{-4}	4×10^{-4}
Reaction time (min)	10	25
Stirring time (min)	5.0	—
Beer's range (ng mL^{-1})	4.0–240	9000–400 000
Ringbom range (ng mL^{-1})	8.0–230	100 000–360 000
Molar absorptivity (L mol^{-1} cm^{-1})	1.22×10^{6}	2.45×10^{3}
Sandell sensitivity (ng cm^{-2})	0.016	12.44
Regression equation		
Slope (μg mL^{-1})	6.21	0.0057
Intercept	0.007	−0.04
Correlation coefficient (r)	0.9988	0.9790
RSD[a] (%)	1.89	3.26
Detection limits (ng mL^{-1})	1.32	2700
Quantification limits (ng mL^{-1})	3.92	8500
Enhancement factor	500	—
Improvement factor	1087	—

[a] Average of 10 determinations for 100 ng per mL Au^{3+} ions.

plotting the transmittance percentage *vs.* the logarithmic value of concentration and found to be in the range of 8.0–230 ng mL^{-1} (Table 2). The enrichment factor, calculated using eqn (2), was found to be 500. The improvement factor was also calculated and found to be 1087. The limits of detection (LOD) and quantification (LOQ) were determined using the $3S_b/m$ and $10S_b/m$ criteria, respectively, where S_b represents the standard deviation of the blank (2.3×10^{-4}) and m signifies the slope of

Table 3 Recovery of gold from spiked water samples using the proposed method

	Proposed method (concentration added)					
	50 ng mL^{-1}		100 ng mL^{-1}		150 ng mL^{-1}	
Sample	Found	Recovery,[a] %	Found	Recovery,[a] %	Found	Recovery,[a] %
Stream water-I[b]	49.4	98.80 ± 0.37	100.8	100.80 ± 0.28	151.7	101.13 ± 0.43
t- and *F*-test	1.53 and 3.18		1.16 and 2.88		1.26 and 2.86	
FAAS method (concentration added)						
	50.9	101.80 ± 0.88	98.2	98.20 ± 0.78	148.3	98.87 ± 0.96
River water-I[c]	50.6	101.20 ± 0.67	99.2	99.20 ± 0.48	149.0	99.33 ± 0.63
t- and *F*-test	1.76 and 3.49		1.32 and 2.74		1.11 and 2.66	
FAAS method (concentration added)						
	48.6	97.20 ± 0.81	102.4	102.40 0.56	152.5	101.67 ± 0.80
Sea water-I[d]	50.8	101.60 ± 0.53	97.9	97.90 ± 0.92	153.2	102.13 ± 0.47
t- and *F*-test	1.47 and 3.05		1.95 and 4.09		1.82 and 3.78	
FAAS method (concentration added)						
	51.0	102.00 ± 0.88	100.9	100.90 ± 0.74	148.8	99.20 ± 0.97
Well water-I[b]	51.4	102.80 ± 0.64	98.2	98.20 ± 0.86	153.6	102.40 ± 0.74
t- and *F*-test	1.91 and 4.05		1.19 and 2.92		1.62 and 3.38	
FAAS method (concentration added)						
	48.9	97.80 ± 0.85	102.8	102.80 ± 0.72	147.2	98.13 ± 0.66
Zamzam water[e]	50.7	101.40 ± 0.93	98.8	98.80 ± 1.15	152.5	101.67 ± 0.89
t- and *F*-test	2.17 and 4.33		1.74 and 3.62		1.87 and 3.98	
FAAS method (concentration added)						
	49.2	98.40 ± 1.22	97.8	97.80 ± 1.07	147.4	98.27 ± 1.19

[a] Mean ± S.D. (n = 6). [b] Collected from Shoubra, Egypt. [c] Collected from Benha, Egypt. [d] Collected from Alexandria, Egypt. [e] Collected from Zamzam, Saudi Arabia.

the calibration curve after extraction (1.5816 ng mL^{-1}). The resulting LOD and LOQ values were 1.30 and 4.92 ng mL^{-1}, respectively. The relative standard deviation (RSD) for ten replicate measurements of a 100 ng per mL Au^{3+} solution was ±1.89%.

3.12. Method validation and application to diverse matrices

To determine the reliability of the IL-USA-DLLME technique, it was employed to quantify Au^{3+} in a variety of sample types, including water, ores, certified reference materials (CRMs), food products, and soil, each containing varying levels of gold.

3.12.1. Analysis of water samples. The optimized protocol was used to measure Au^{3+} ions in water samples collected from a stream and well (Shoubra, Egypt), the Nile River, seawater (Alexandria, Egypt), and the Zamzam Well (Saudi Arabia). Method dependability was verified through spiking experiments and parallel analyses. The findings obtained from these four distinct water sources are presented in Table 3. Recovery studies, performed using spiked samples, demonstrated the ability of the developed method to accurately measure Au^{3+} ions. The recovery rates for the added standard solutions consistently exceeded 98.2%, validating the method's accuracy and indicating minimal influence from the sample matrix.

The effectiveness of the developed method was further evaluated by comparing its performance with flame atomic absorption spectrometry (FAAS) using *t*-tests (for assessing accuracy) and *F*-tests (for assessing precision).[71] Mean values were compared using Student's *t*- and *F*-tests at a 95% confidence level with five degrees of freedom. The results, as shown in (Table 3), indicated that the calculated values did not surpass the corresponding theoretical values. The suggested method offers several advantages over other techniques, including a broader application range, enhanced stability, reduced analysis time, and improved accuracy.

3.12.2. Analysis of mineral specimens. The developed methodology was employed for the analysis of mineral samples. To evaluate the precision of the proposed technique, standard addition experiments were performed. Varying quantities of gold ions were introduced into 25 mL aliquots of prepared solid samples, which were then subjected to the IL-USA-DLLME process. The resulting data are presented in (Table 4).

3.12.3. Analysis of certified geochemical reference materials. The described procedure was utilized to quantify Au^{3+} in several certified geochemical reference materials (GAUs 15–17), with the results compiled in Table 5. The extraction performance was enhanced, with minimal matrix interference observed. The measured values were compared with those obtained using flame atomic absorption spectrometry (FAAS), demonstrating acceptable concordance.

Table 4 Determination of Au (μg g^{-1}) ore samples (*n*: 3)

	[Au (μg g^{-1})]	
Sample type	Proposed	FAAS
Ore-1 (Wadi El-Natrun, Egypt)	22.6 ± 0.7	22.9 ± 1.5
Ore-2 (Abo-Tartoor, Egypt)	61.4 ± 1.3	61.0 ± 2.1
Ore-3 (Al-Areesh, Egypt)	12.6 ± 0.7	12.8 ± 1.1

Table 5 Determination of Au^{3+} in geochemical reference samples

		Found[a] (%)			
Sample	Certified (μg g^{-1})	PM	FAAS	*t*-Test[b]	*F*-Value[c]
GAU 15	0.30 ± 0.01	0.29 ± 0.06	0.28 ± 0.12	1.42	3.27
GAU 16	1.09 ± 0.04	1.11 ± 0.08	1.08 ± 0.20	1.64	3.87
GAU 17	3.14 ± 0.08	3.15 ± 0.10	3.17 ± 0.24	1.27	3.02

[a] Mean ± standard deviation ($n = 6$). [b] Tabulated *t*-value for five degrees of freedom at *P* (0.95) is 2.57. [c] Tabulated *F*-value at *P* (0.95) is 5.05.

3.12.4. Analysis of food matrices and soil samples. To validate the dependability of the proposed methodology, it was applied to the determination of trace amounts of Au^{3+} in a range of real-world food samples (Table 6). The initial analysis confirmed that the natural gold level is lower than the detection limit, and then spiked gold levels were examined. To confirm the accuracy of the developed method, recovery studies were also conducted by fortifying the samples with different gold concentrations prior to any sample preparation steps. The obtained results are summarized in Table 6. Recovery rates ranging from 98.8% to 101.5% were achieved, confirming the reliability of the proposed technique.

In a bid to showcase the applicability of the method, it was extended to the colorimetric detection of Au^{3+} ions in a soil sample (Table 6). The sample was analyzed using the proposed approach. The potential interferences from co-extracted contaminants (*e.g.*, cyanide and mercury) were assessed and found to be negligible. To validate the method, samples were spiked with varying Au^{3+} quantities and subsequently analyzed. This outcome firmly establishes the proposed method as reliable and robust. Student's *t*- and *F*-tests were conducted on the mean values at a 95% confidence level with five degrees of freedom.[71] The results indicated that the calculated values did not significantly deviate from the theoretical values, signifying no substantive distinction from the compared procedure.

Table 6 Analysis of gold in food and soil samples

			Found[a] (ng g^{-1})			
Sample	Real ng g^{-1}	Added ng g^{-1}	Proposed	FAAS	*t*-Test[b]	*F*-Value[c]
Fish	—	50	49.8	49.7	1.63	3.43
		100	100.2	99.7		
		150	149.3	150.6	1.48	3.11
		200	200.8	199.1		
Shrimp	—	60	59.9	60.2	1.84	3.76
		120	120.7	121.2		
		180	179.2	181.4	1.76	3.39
		240	238.8	241.5		
Soil	—	40	39.9	39.8	1.26	2.86
		80	80.3	69.6		
		160	159.3	161.5	1.55	3.47
		200	201.2	197.7		

[a] Average of six determinations. [b] Tabulated *t*-value for five degrees of freedom at *P* (0.95) is 2.57. [c] Tabulated *F*-value at *P* (0.95) is 5.05.

Table 7 Comparison of different methods for determination of gold in aqueous samples

Method	EF[a]	LOD ng mL^{-1}	RSD (%)	Linear range ng mL^{-1}	Ref.
UAE-DLLME[b]-ETAAS	220	0.008	4.2	0.075–0.75	72
SPE-ICP-OES	150	0.32	3.3	—	31
DLLME-GFAAS	388	0.005	4.2	0.03–0.5	73
CPE[c]-ICP-OES	8.6	0.5	<5.0	0.5–1000	29
SPE[d]-FAAS	—	0.8	1.7	50–34 000	74
DLLME-ICP-OES	149	0.09	6.0	0.3–100	75
USAE-SFODMS[e]-FAAS	34.8	0.45	1.68	1.5–400	76
SPE-spectrophotometry	100	6.1	2.51	80–1240	77
HFLPME[f]-FAAS	50	0.9	2.17	3.0–170	78
CPE-FAAS	16	3.8	1.95	4.0–500	79
SsLLME[g]-FAAS	60	1.5	—	—	80
SPE-FAAS	200	13	—	—	81
FI-spectrophotometry		30	2.67	100–12 000	82
SPE-FAAS	31	1.61	2.05		22
IP-DLLME[h]/FAAS	40	1.8	2.27	8.0–100	83
IL-USA-DLLME-colorimetry	500	1.32	1.87	4.0–240	This work

[a] Enrichment factor. [b] UAE: ultrasound-assisted emulsification; DLLME: dispersive liquid–liquid microextraction. [c] CPE: cloud point extraction. [d] SPE: solid-phase extraction. [e] USAE-SFODMS: ultrasound-assisted emulsification of solidified locating organic drops. [f] Hollow fiber liquid phase microextraction. [g] Supramolecular solvent-based liquid–liquid microextraction. [h] Ion-pair dispersive liquid–liquid microextraction.

3.13. Comparison of the IL-USA-DLLME technique with alternative approaches

A comparative analysis of the present method with other reported preconcentration and extraction techniques for gold determination[22,29,31,72–83] is presented in (Table 7). The IL-USA-DLLME procedure offers several benefits, including a rapid extraction time (within 5.0 minutes), operational simplicity, high sensitivity, cost-effectiveness, a substantial enrichment factor (500), a low detection limit (1.30 ng mL^{-1}), and minimal consumption of organic solvent (200 μL), aligning with principles of environmentally conscious chemistry. The described procedure exhibits superior quantification capabilities, a broad linear working range, and a high enrichment factor when compared to various other established methods. The proposed method improves real-world gold detection compared to existing green techniques (*e.g.*, toxicity reduction, cost, and accessibility). In this study, the extraction performance of the developed procedure was evaluated in the presence of appropriate concentrations of nickel, manganese, cobalt, cadmium, copper, zinc, lead, platinum, iron, and palladium. Among these metal ions, the method demonstrated exceptional selectivity for gold ions at extremely low concentrations. Consequently, the advanced IL-USA-DLLME technique can serve as a viable alternative for the analysis of gold in various environmental liquid and solid matrices (Table 7).

4 Conclusion

Ultrasonic irradiation effectively accelerated the formation of the turbid dispersive extraction mixture, achieving this within a brief 2 minute period. The IL-USA-DLLME technique significantly reduces sample preparation time and the use of volatile organic solvents. Unlike conventional DLLME, this method is solvent-minimized, avoiding the need for a separate dispersing solvent. The use of [Omim][TF$_2$N] as the extracting solvent eliminates the requirement for chilling with an ice bath to induce turbidity. The Au^{3+} complex demonstrates improved performance within the IL-USA-DLLME framework. This method is characterized by its simplicity, speed, and reproducibility. It can be applied to both qualitative and quantitative analysis of Au^{3+}, utilizing small sample volumes and micro-scale amounts of [Omim][TF$_2$N]. The substantial enrichment factor, combined with straightforward operation, represents another key advantage. The proposed technique exhibits low detection and quantification limits, comparable to or surpassing those of other methods used for gold species determination, and offers an enhanced calibration range with reduced sample consumption. The calibration curve is linear over the concentration range of 4.0–240 ng mL^{-1} whereas applying the Ringbom method it gave a more accurate range from 8.0–230 ng mL^{-1}. The proposed method exhibits remarkably low limits for both detection and quantification, measured at 1.30 and 3.92 ng mL^{-1}, respectively. Consequently, this procedure is particularly advantageous for routine analytical applications. Cooling during centrifugation facilitates the continuous formation of minute extractant phase droplets, concentrating the extracted analytes at the bottom of the centrifuge tube, enabling continuous operation and potential automation.

Data availability

All data and materials should be available upon request.

Author contributions

Fahad Alminderej and Alaa Younis: conceptualization, methodology, data curation, investigation, supervision, validation, writing – original draft, and writing – review & editing. Alaa Amin and Hesham El-Feky: conceptualization, supervision, investigation, methodology, visualization, validation, and writing – original draft & editing.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors' sincere thanks are due to Qassim University (Saudi Arabia) and Benha University (Egypt) for providing the necessary facilities.

References

1 World Gold Council, *The world of gold*, **https://www.gold.org/index/html**, 22 August, 2005.

2 N. V. Fomchenko, T. F. Kondrat'eva and M. I. Muravyov, A new concept of the biohydrometallurgical technology for gold recovery from refractory sulfide concentrates, *Hydrometallurgy*, 2016, **164**, 78–82, DOI: **10.1016/j.hydrome2016.05.011**.

3 A. Aworn, P. Thiravetyan and W. Nakbanpote, Recovery of gold from gold slag by wood shaving fly ash, *J. Colloid Interface Sci.*, 2005, **287**, 394–400, DOI: **10.1016/j.jcis.2005.02.048**.

4 Y. Qiang, S. Gao, M. Wu, X. Lei and H. Fang, A new suggestion to marine gold extraction: utilizing reduced graphene oxide membranes within seawater desalination processes, *Sci. Total Environ.*, 2024, **947**, 174602, DOI: **10.1016/j.scitotenv.2024.174602**.

5 M. D. Ye and M. J. Lin, Determination of trace gold by flow injection on-line preconcentration flame atomic absorption spectrometry with trioctylamine levextrel resin, *Spectrosc. Spectral Anal.*, 2004, **24**, 1270–1272, PMID: 15760040.

6 T. Itagaki, T. Ashino and K. Takada, Determination of trace amounts of gold and silver in high-purity iron and steel by electrothermal atomic absorption spectrometry after reductive coprecipitation, *Fresenius. J. Anal. Chem.*, 2000, **368**, 344–349, DOI: **10.1007/s002160000455**.

7 M. Soylak, L. Elci and M. Dogan, A sorbent extraction procedure for the preconcentration of gold, silver and palladium on an activated carbon column, *Anal. Lett.*, 2000, **33**, 513–525, DOI: **10.1080/00032710008543070**.

8 M. S. El-Shahawi, A. S. Bashammakh and O. S. Bahaffi, Chemical speciation and recovery of gold (I,III) from wastewater and silver by liquid–liquid extraction with the ion-pair reagent amiloride mono hydrochloride and AAS determination, *Talanta*, 2007, **72**, 1494–1499, DOI: **10.1016/j.talanta.2007.01.057**.

9 Z. Bahadır, V. N. Bulut, A. Mermer, N. Demirbaş, C. Duran and M. Soylak, The separation–preconcentration and determination of ultra-trace gold in water and solid samples by dispersive liquid–liquid microextraction using 4-ethyl-1(2-(4-(4-nitrophenyl)piperazin-1-yl)acetyl) thiosemicarbazide as chelating agent and flame atomic absorption spectrometry, *J. Iran. Chem. Soc.*, 2018, **15**, 1347–1354, DOI: **10.1007/s13738-018-1333-z**.

10 J. L. Manzoori, H. Abdolmohammad-Zadeh and M. Amjadi, Simplified cloud point extraction for the preconcentration of ultra-trace amounts of gold prior to determination by electrothermal atomic absorption spectrometry, *Microchim. Acta*, 2007, **159**, 71–78, DOI: **10.1007/s00604-006-0727-2**.

11 P. Pohl and B. Prusisz, On the applicability of duolite GT-73 to column preconcentration of gold and palladium prior to determination by inductively coupled plasma atomic emission spectrometry, *Microchim. Acta*, 2005, **150**, 159–165, DOI: **10.1007/s00604-005-0343-6**.

12 H. E. H. Ahmed and M. Soylak, A novel nanomotor (ZIF-L(Co)/WSe$_2$ nano-composite) for nanomotor motion-based dispersive micro-solid phase extraction (NM-d-μSPE) of gold and palladium, *Talanta*, 2025, **293**, 128072, DOI: **10.1016/j.talanta.2025.128072**.

13 M. Konecna and J. Komarek, Utilization of electrodeposition for electro-thermal atomic absorption spectrometry determination of gold, *Spectrochim. Acta, Part B*, 2007, **62**, 283–287, DOI: **10.1016/j.sab.2006.12.010**.

14 F. Habashi, Gold-An Historical Introduction, *Gold Ore Processing*, Elsevier, 2016, pp. 1–20.

15 A. Hajinia and T. Heidari, Sensitive fluorometric determination of gold in geological samples using free assay pre-concentration coupled with microfluidic paper-based analytical device, *Microchem. J.*, 2021, **164**, 105923, DOI: **10.1016/j.microc.2021.105923**.

16 S. Pessanha, I. Queralt, M. L. Carvalho and J. M. Sampaio, Determination of gold leaf thickness using X-ray fluorescence spectrometry: accuracy compare-son using analytical methodology and Monte Carlo simulations, *Appl. Radiat. Isot.*, 2019, **152**, 6–10, DOI: **10.1016/j.apradiso.2019.06.014**.

17 J. V. Mattioni, D. S. Franciscato, L. M. Sihn and H. E. Toma, Analytical determination of gold ions based on ranelate induced nanoparticle formation, *Anal. Methods*, 2022, **14**, 1698–1704, DOI: **10.1039/d2ay00411a**.

18 S. Thanomsak, C. Insombat, P. Chaiyo, T. Tuntulani and W. Janrungroatsakul, Fabrication of a paper-based sensor from graphene quantum dots coated with a polymeric membrane for the determination of gold(III) ions, *Anal. Methods*, 2021, **13**, 4785–4792, DOI: **10.1039/D1AY01258D**.

19 V. Solis-Tinoco, A. Acevedo-Barrera, O. Vazquez-Estrada, M.-J. Cervantes, N. Hernandez-Como, L. F. Olguin and A. Garcia-Valenzuela, Fast and accurate optical determination of gold-nanofilms thickness, *Opt. Laser Technol.*, 2021, **134**, 106604, DOI: **10.1016/j.optlastec.2020.106604**.

20 Y.-T. Chuang, J.-R. Liou, Y.-Y. Chao, Y.-H. Lin, T.-Y. Wu and Y.-L. Chen, Multivariate optimization of large-volume sample stacking with polarity switching by capillary electrophoresis for determination of gold nanoparticle size, *Microchem. J.*, 2022, **178**, 107387, DOI: **10.1016/j.microc.2022.107387**.

21 W. A. Soomro, M. Y. Khuhawar, T. M. Jahangir, M. F. Lanjwani, Z. A. Bhatti, R.-Z. Brohi and I. K. Rind, Development of a dispersive liquid–liquid microextraction technique for ultra-sensitive detection of gold in environmental samples using atomic absorption spectrometry, *Environ. Monit. Assess.*, 2025, **197**, 235, DOI: **10.1007/s10661-025-13684-5**.

22 N. S. Medvedev, V. D. Kurbatova, A. O. Frolova and T. Y. Guselnikova, Elemental analysis with sorption preconcentration by graphene oxide for mineral water by inductively coupled plasma–optical emission and mass spectrometries (ICP-OES and ICP-MS), *Anal. Lett.*, 2025, **58**, 1166–1181, DOI: **10.1080/00032719.2024.2356759**.

23 C. S. Provete, B. M. Dalfior, R. Mantovaneli, M. Tereza, W. D. Carneiro and G. P. Brandao, Comparison of the performance of ICP-MS, CV-ICP-OES, and TDA AAS in determining mercury in marine sediment samples, *ACS Omega*, 2024, **9**, 49229–49238, DOI: **10.1021/acsomega.4c06144**.

24 V. N. Losev, V. V. Parfenova, E. V. Elsufev, E. V. Borodina, S. I. Metelitsa and A. K. Trofimchuk, Separation and preconcentration followed by ICP-OES and ICP-MS determination of precious metals using silica gel chemically modified with dithiocarbamate groups, *Sep. Sci. Technol.*, 2020, **55**, 2659–2669, DOI: **10.1080/01496395.2019.1655454**.

25 Z. Chen, B. Chen, M. He, H. Wang and B. Hu, A porous organic polymer with magnetic nanoparticles on a chip array for preconcentration of platinum (IV), gold(III) and bismuth(III) prior to their on-line quantitation by ICP-MS, *Microchim. Acta*, 2019, **186**, 107, DOI: **10.1007/s00604-018-3139-1**.

26 P. Liang, E. Zhao, Q. Ding and D. Du, Application of dispersive liquid–liquid microextraction and high-performance liquid chromatography for the determination of three phthalate esters in water samples, *Spectrochim. Acta, Part B*, 2008, **63**, 714–717, DOI: **10.1016/j.sab.2008.04.002**.

27 J. Dobrzyńska, M. Dąbrowska, R. Olchowski and R. Dobrowolski, An ion-imprinted thiocyanato-functionalized mesoporous silica for preconcentration of gold(III) prior to its quantitation by slurry sampling graphite furnace AAS, *Microchim. Acta*, 2018, **185**, 564–569, DOI: **10.1007/s00604-018-3106-x**.

28 N. Jalilian, H. Ebrahimzadeh, A. A. Asgharinezhad and K. Molaei, Extraction and determination of trace amounts of gold(III), palladium(II), platinum(II) and silver(I) with the aid of a magnetic nanosorbent made from Fe_3O_4-decorated and silica-coated graphene oxide modified with a polypyrrole-polythiophene copolymer, *Microchim. Acta*, 2017, **184**, 2191–2200, DOI: **10.1007/s00604-017-2170-y**.

29 H. B. Senturk, A. Gundogdu, V. N. Bulut, C. Duran, M. Soylak, L. Elci and M. Tufekci, Separation and enrichment of gold (III) from environmental samples prior to its flame atomic absorption spectrometric determination, *J. Hazard. Mater.*, 2007, **149**, 317–323, DOI: **10.1016/j.jhazmat.2007.03.083**.

30 S. Chen, X. Zhu and Z. Miner, Simplified cloud point extraction-inductively coupled plasma mass spectrometry for the preconcentration/analysis of ultra-trace gold, *Miner. Eng.*, 2010, **23**, 1152–1154, DOI: **10.1016/j.mineng.2010.07.009**.

31 M. Soylak and M. Tuzen, Coprecipitation of gold(III), palladium(II) and lead(II) for their flame atomic absorption spectrometric determinations, *J. Hazard. Mater.*, 2008, **152**, 656–661, DOI: **10.1016/j.jhazmat.2007.07.027**.

32 L. Zhang, L. Zhenhua, H. Zheng and C. Xijun, Solid phase extraction of gold (III) on attapulgite modified with triocarbohydrazide prior to its determination in environmental samples by ICP-OES, *Spectrochim. Acta, Part A*, 2011, **79**, 1234–1239, DOI: **10.1016/j.saa.2011.04.048**.

33 A. Iraji, D. Afzali and A. Mostafavi, Separation for trace amounts of gold (III) ion using ion-pair dispersive liquid–liquid microextraction prior to flame atomic absorption spectrometry determination, *Int. J. Environ. Anal. Chem.*, 2013, **93**, 315–324, DOI: **10.1080/03067319.2011.609937**.

34 M. Rezaee, Y. Assadi, M. R. Milani Hosseini, E. Aghaee, F. Ahmadi and S. Berijani, Determination of organic compounds in water using dispersive liquid–liquid microextraction, *J. Chromatogr. A*, 2006, **1116**, 1–9, DOI: **10.1016/j.chroma.2006.03.007**.

35 S. Kagaya, D. Takata, T. Yoshimori, T. Kanbara and K. Tohda, A sensitive and selective method for determination of gold(III) based on electrothermal atomic absorption spectrometry in combination with dispersive liquid–liquid microextraction using dicyclohexylamine, *Talanta*, 2010, **80**, 1364–1370, DOI: **10.1016/j.talanta.2009.09.037**.

36 S. Keskin, D. K. Talay, U. Akman and O. Hortac, A review of ionic liquids towards supercritical fluid applications, *J. Supercrit. Fluids*, 2007, **43**, 150–180, DOI: **10.1016/j.supflu.2007.05.013**.

37 H. Zhao, S. Xia and P. Ma, Review: use of ionic liquids as green solvents for extractions, *J. Chem. Technol. Biotechnol.*, 2005, **80**, 1089–1096, DOI: **10.1002/jctb.1333**.

38 C. Chiappe and D. Pieraccini, Review commentary; ionic liquids: solvent properties and organic reactivity, *J. Phys. Org. Chem.*, 2005, **18**, 275–297, DOI: **10.1002/poc.863**.

39 D. S. Junior, F. J. Krug, M. D. G. Pereira and M. Korn, Currents on ultrasound-assisted extraction for sample preparation and spectroscopic analytes determination, *Appl. Spectrosc. Rev.*, 2006, **41**, 305–321, DOI: **10.1080/05704920600620436**.

40 K. Ashley, R. N. Andrews, L. Cavazos and M. Demange, Ultrasonic extraction as a sample preparation technique for elemental analysis by atomic spectrometry, *J. Anal. At. Spectrom.*, 2001, **16**, 1147–1153, DOI: **10.1039/B102027G**.

41 A. Heintz, Recent developments in thermodynamics and thermophysics of nonaqueous mixtures containing ionic liquids, *J. Chem. Thermodyn.*, 2005, **37**, 525–535, DOI: **10.1016/j.jct.2005.04.003**.

42 M. Ghaedi, A. Shokrollahi, A. H. Kianfar, A. S. Mirsadeghi, A. Pourfarokhi and M. Soylak, The determination of some

heavy metals in food samples by flame atomic absorption spectrometry after their separation-preconcentration on bissalicylaldehyde,1,3 propandiimine (BSPDI) loaded on activated carbon, *J. Hazard. Mater.*, 2008, **154**, 128–134, DOI: **10.1016/j.jhazmat.2007.10.003**.

43 M. Ghaedi, Pyrimidine-2-thiol as selective and sensitive ligand for preconcentration and determination of Pb^{2+}, *Chem. Anal.*, 2006, **51**, 593–602, **https://beta.chem.uw.edu.pl/chemanal/**.

44 S. Li, S. Cai, W. Hu, H. Chen and H. Liu, Ionic liquid-based ultrasound-assisted dispersive liquid–liquid microextraction combined with electrothermal atomic absorption spectrometry for a sensitive determination of cadmium in water samples, *Spectrochim. Acta, Part B*, 2009, **64**, 666–671, DOI: **10.1016/j.sab.2009.05.023**.

45 A. B. Shaikh, S. H. Gaikwad and U. B. Barache, A new experimental design for liquid-liquid extractive spectrophotometric determination of gold(III) using 4-(4′-flurobenzylideneimino)-3-methyl-5-mercapto-1,2,4-triazole, *Anal. Chem. Lett.*, 2020, **10**, 336–356, DOI: **10.1080/22297928.2020.1776634**.

46 D. G. Themelis, A. V. Trellopoulos, P. D. Tzanavaras and M. Sofoniou, Highly selective flow injection spectrophotometric determination of gold based on its catalytic effect on the oxidation of variamine blue by potassium iodate in aqueous *N*,*N*-dimethylformamide medium, *Talanta*, 2007, **72**, 277–281, DOI: **10.1016/j.talanta.2006.10.031**.

47 M. Gangadharappa, R. P. Raveendra, R. V. Krishna and R. T. Sreenivasulu, Solid phase extraction and a spectrophotometric method for the determination of trace amounts of gold with 4-rhodanineazo benzoic acid, *J. Indian Chem. Soc.*, 2004, **81**, 525–527.

48 Z. J. Li, J. M. Pan and J. Tang, Highly sensitive and selective spectrophotometric method for determination of trace gold in geological samples with 5-(2-hydroxy-5-nitrophenylazo) rhodanine, *Anal. Bioanal. Chem.*, 2003, **375**, 408–413, DOI: **10.1007/s00216-002-1714-z**.

49 B. R. Hyun, S. V. Dzyuba, R. A. Bartsch and E. L. Quitevis, Intermolecular dynamics of room-temperature ionic liquids: femto-second optical Kerr effect measurements on 1-alkyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl) imides, *J. Phys. Chem. A*, 2002, **106**, 7579–7585, DOI: **10.1021/jp0141575**.

50 G. T. Wei, Z. Yang and C. J. Chen, Room temperature ionic liquid as a novel medium for liquid/liquid extraction of metal ions, *Anal. Chim. Acta*, 2003, **488**, 183–192, DOI: **10.1016/S0003-2670(03)00660-3**.

51 S. V. Dzyuba and R. A. Bartsch, Influence of structural variations in 1-alkyl(aralkyl)-3-methylimidazoliumhexafluorophosphates and bis(trifluoromethylsulfonyl)imides on physical properties of the ionic liquids, *ChemPhysChem*, 2002, **3**, 161–166, DOI: **10.1002/1439-7641(20020215)3:2<161::AID-CPHC161>3.0.CO;2-3**.

52 A. S. Amin, M. A. Kassem and S. M. N. Moalla, Determination of scandium in monazite and environmental samples using cloud point extraction coupled with a spectrophotometric technique, *RSC Adv.*, 2016, **6**, 73797–73804, DOI: **10.1039/C6RA10049J**.

53 S. Eid, A. A. Abdelwahab, A. S. Amin and H. H. El-Feky, An innovative eco-friendly optical sensor designed specifically to detect lanthanum ions in environmental samples, *Spectrosc. Lett.*, 2025, **58**, 1–14, DOI: **10.1080/00387010.2025.2482732**.

54 B. Hu, M. He, B. Chen and L. Xia, Liquid phase microextraction for the analysis of trace elements and their speciation, *Spectrochim. Acta, Part B*, 2013, **86**, 14–30, DOI: **10.1016/j.sab.2013.05.025**.

55 I. Silachyov, V. A. Glagolev and M. N. Kokkuzova, Gold content determination in small core-samples by instrumental neutron activation analysis, *Int. J. Biol. Chem.*, 2024, **17**, 78–88, DOI: **10.26577/IJBCh2024v17i1-a9**.

56 H. Liu, G. Beaudoin, S. Makvandi and S. E. Jackson, Multivariate statistical analysis of trace element compositions of native gold from orogenic gold deposits: implication for mineral exploration, *Ore Geol. Rev.*, 2021, **131**, 104061, DOI: **10.1016/j.oregeorev.2021.104061**.

57 J. Zhang, Y. Cui, T. Zhou, J. Wang, Z. Zhu and F. Liu, Development of certified reference materials of trace elements in gold solution (GBW02797–GBW02800), *Accredit. Qual. Assur.*, 2023, **28**, 99–310, DOI: **10.1007/s00769-023-01557-8**.

58 K. Pyrzyńska, Recent developments in the determination of gold by atomic spectrometry techniques, *Spectrochim. Acta, Part B*, 2005, **60**, 1316–1322, DOI: **10.1016/j.sab.2005.06.010**.

59 X. Tang, B. Li, J. Lu, H. Liu and Y. Zhao, Gold determination in soil by ICP-MS: comparison of sample pretreatment methods, *J. Anal. Sci. Technol.*, 2020, **11**, 45–53, DOI: **10.1186/s40543-020-00245-3**.

60 J. Dupont, C. S. Consorti and J. Spencer, Room-temperature molten salts: neoteric green solvents for chemical reactions and processes, *J. Braz. Chem. Soc.*, 2000, **11**, 337–344, DOI: **10.1590/S0103-50532000000400002**.

61 F. Mutelet, V. Butet and J. N. Jaubert, Application of inverse gas chromatography and regular solution theory for characterization of ionic liquids, *Ind. Eng. Chem. Res.*, 2005, **44**, 4120–4127, DOI: **10.1021/ie048806l**.

62 S. N. V. K. Aki, J. F. Brennecke and A. Samanta, How polar are room temperature ionic liquids, *Chem. Commun.*, 2001, **5**, 413–414, DOI: **10.1039/B008039J**.

63 P. Liang, J. Xu and Q. Li, Application of dispersive liquid–liquid microextrac-tion and high-performance liquid chromatography for the determination of three phthalate esters in water samples, *Anal. Chim. Acta*, 2008, **609**, 53–58, DOI: **10.1016/j.aca.2007.12.025**.

64 M. T. Naseri, P. Hemmatkhah, M. R. M. Hosseini and Y. Assadi, Combination of dispersive liquid–liquid microextraction with flame atomic absorption spectrometry using microsample introduction for determination of lead in water samples, *Anal. Chim. Acta*, 2008, **610**, 135–141, DOI: **10.1016/j.aca.2008.01.020**.

65 D. K. Dubey, D. Pardasani, A. K. Gupta, M. Palit, P. K. Kanaujia and V. Tak, Hollow fiber-mediated liquid-

phase microextraction of chemical warfare agents from water, *J. Chromatogr. A*, 2006, **1107**, 29–35, DOI: 10.1016/j.chroma.2005.12.095.

66 J. F. Peng, J. F. Liu, X. Hu and G. B. Jiang, Direct determination of chloro-phenols in environmental water samples by hollow fiber supported ionic liquid membrane extraction coupled with high-performance liquid chromatography, *J. Chromatogr. A*, 2007, **1139**, 165–170, DOI: 10.1016/j.chroma.2006.11.006.

67 M. Baghdadi and F. Shemirani, In situ solvent formation microextraction based on ionic liquids: a novel sample preparation technique for determination of inorganic species in saline solutions, *Anal. Chim. Acta*, 2009, **634**, 186–191, DOI: 10.1016/j.aca.2008.12.017.

68 C. Jungnickel, J. Luczak, J. Ranke, J. F. Fernandez, A. Muller and J. Thoming, Micelle formation of imidazolium ionic liquids in aqueous solution, *Colloids Surf., A*, 2008, **316**, 278–284, DOI: 10.1016/j.colsurfa.2007.09.020.

69 B. Dong, X. Zhao, L. Zheng, J. Zhang, N. Li and T. Inoue, Aggregation behavior of long-chain imidazolium ionic liquids in aqueous solution: micellization and characterization of micelle microenvironment, *Colloids Surf., A*, 2008, **317**, 666–672, DOI: 10.1016/j.colsurfa.2007.12.001.

70 G. Somer, Ş. Kalaycı and O. Şendil, A new and direct method for the determination of trace elements in spinach using differential pulse polarography, *J. Electroanal. Chem.*, 2016, **778**, 49–52, DOI: 10.1016/j.jelechem.2016.07.041.

71 J. N. Miller and J. C. Miller, *Statistics and Chemometrics for Analytical Chemistry*, Prentice Hall, England, 5th edn, 2005.

72 S. Z. Mohammadi, D. Afzali, M. A. Taher and Y. M. Baghelania, Determination of trace amounts of palladium by flame atomic absorption spectrometry after ligandless-dispersive liquid–liquid microextraction, *Microchim. Acta*, 2010, **168**, 123–128, DOI: 10.1007/s00604-009-0267-7.

73 M. Shamsipour and M. Ramezani, Selective determination of ultra trace amounts of gold by graphite furnace atomic absorption spectrometry after dispersive liquid–liquid microextraction, *Talanta*, 2008, **75**, 294–300, DOI: 10.1016/j.talanta.2007.11.009.

74 F. Sabermahani, M. A. Taher and H. Bahrami, Separation and pre-concentration of trace amounts of gold from water samples prior to determination by flame atomic absorption spectrometry, *Arabian J. Chem.*, 2016, **9**, S1700–S1705, DOI: 10.1016/j.arabjc.2012.04.053.

75 J. Hassan, N. Zari, K. Tabar-Heydar and S. H. Ahmadi, Ion-association dispersive liquid–liquid microextraction of ultra-trace amount of gold in water samples using Aliquat 336 prior to inductively coupled plasma atomic emission spectrometry determination, *J. Anal. Sci. Technol.*, 2016, **7**, 22–27, DOI: 10.1186/s40543-016-0102-9.

76 S. Tajic and M. A. Taher, New method for microextraction of ultra-trace quantities of gold in real samples using ultrasound-assisted emulsification of solidified floating organic drops, *Microchim. Acta*, 2011, **173**, 249–257, DOI: 10.1007/s00604-011-0553-z.

77 A. S. Amin, Utility of solid phase extraction for spectrophotometric determination of gold in water, jewel and ore samples, *Spectrochim. Acta, Part A*, 2010, **77**, 1054–1058, DOI: 10.1016/j.saa.2010.08.072.

78 C. Zeng and L. Tang, Determination of gold by flame atomic absorption spectrometry with hollow fiber liquid phase microextraction using room temperature ionic liquids, *Anal. Lett.*, 2013, **46**, 1442–1453, DOI: 10.1080/00032719.2013.766799.

79 S. Tong, Q. Jia, N. Song, W. Zhou, T. Duan and C. Bao, Determination of gold(III) and palladium(II) in mine samples by cloud point extraction preconcentration coupled with flame atomic absorption spectrometry, *Microchim. Acta*, 2011, **172**, 95–102, DOI: 10.1007/s00604-010-0466-2.

80 E. Yilmaz and M. Soylak, Supramolecular solvent microextraction of gold prior to its determination by microsample injection system coupled with flame atomic absorption spectrometry, *RSC Adv.*, 2014, **4**, 47396–47401, DOI: 10.1039/C4RA08209E.

81 M. Karimi, V. Amani, F. Aboufazeli, H. R. L. Z. Zhad, O. Sadeghi and E. Najafi, Flame atomic absorption determination of gold ion in aqueous samples after preconcentration using 9-acridinylamine functionalized γ-alumina nano-particles, *J. Chem.*, 2013, 142845, DOI: 10.1155/2013/142845.

82 D. G. Themelis, A. V. Trellopoulos, P. D. Tzanavaras and M. Sofoniou, Highly selective flow injection spectrophotometric determination of gold based on its catalytic effect on the oxidation of variamine blue by potassium iodate in aqueous *N*,*N*-dimethylformamide medium, *Talanta*, 2007, **72**, 277–281, DOI: 10.1016/j.talanta.2006.10.031.

83 A. Hol, A. A. Kartal, A. Akdogan, A. Elçi and T. L. Arslan, Ion pair-dispersive liquid-liquid microextraction coupled to microsample injection system-flame atomic absorption spectrometry for determination of gold at trace level in real samples, *Acta Chim. Slov.*, 2015, **62**, 196–203, DOI: 10.17344/acsi.2014.897.