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Green *in situ* ionic liquid-based microextraction for selective determination and operational speciation of Cr(III) and Cr(VI) in environmental and biological samples: a sustainable analytical approach

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A pyridinium based-task-specific ionic liquid was successfully synthesized and characterized. Subsequently, an *in situ* solvent formation microextraction technique using the synthesized task-specific ionic liquid, coupled with atomic absorption spectrometry, was developed for the selective determination and operational speciation of Cr(III) and Cr(VI) species in various water and urine samples. The microextraction procedure for chromium ions was performed through the complexation of chromium ions with the ionic liquid 1-(2-bromoethyl)pyridinium bromide functionalized with 8-hydroxyquinoline to form a task-specific ionic liquid (1-(2-(quinolin-8-yloxy)ethyl)pyridinium bromide), abbreviated as [QPy][Br]. Subsequently, the complexation of [QPy][Br] with chromium ions in an aqueous medium was carried out, followed by the addition of hexafluorophosphate as a counter ion to the extraction system to induce an *in situ* metathesis reaction, producing the hydrophobic (water-immiscible) ionic liquid [QPy][PF_6], thereby enabling phase separation. Several experimental parameters affecting the microextraction system were optimized using multivariate response surface methodology. The resulting mathematical equations were employed to construct response surface plots for predicting the extraction behavior of the chromium ions and determining the optimum extraction conditions. Under the optimized conditions, the calibration curves exhibit linearity within the ranges of 100–500 and 10–1000 ng L^{-1}, limits of detection of 20.6 and 4.8 ng L^{-1}, and relative standard deviations for seven replicate determinations of 3.1% and 2.6% for Cr(III) and Cr(VI), respectively. Finally, the developed method was successfully applied to the microextraction and determination of chromium ions in several water and urine samples, yielding satisfactory recoveries. The term speciation in this work refers to an operational chemical discrimination based on selective extraction behavior rather than instrumental separation.

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Sustainability spotlight

This work presents a green *in situ* ionic liquid-based microextraction strategy for the selective determination and operational speciation of Cr(III) and Cr(VI) in environmental and biological samples. The method follows green chemistry principles by eliminating volatile organic solvents through the *in situ* formation of a task-specific ionic liquid within the sample matrix, reducing hazardous waste and improving laboratory safety. The microextraction approach enables method miniaturization, leading to lower sample and reagent consumption while maintaining high analytical performance. Response surface methodology was used to optimize extraction conditions, ensuring high efficiency with minimal chemical and energy requirements. Overall, this sustainable analytical platform provides a sensitive, efficient, and environmentally benign alternative for chromium speciation and supports the development of greener analytical methodologies.

Introduction

Recently, the application of ionic liquids (ILs), especially room-temperature ionic liquids (RTLs), in various fields of chemistry, particularly in the separation and extraction of organic and inorganic species, has significantly increased due to their unique properties, such as ease of synthesis, low vapour pressure, low melting point, high boiling point and thermal stability, wide liquid-phase temperature range, non-flammability, low toxicity and tunable physiochemical properties.[1,2] These

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characteristics have made ionic liquids highly attractive compounds in various fields of chemistry, particularly analytical chemistry, where ILs have progressively found applications ranging from sample preparation techniques to electrochemical analyses.[3] Over the last decade, ionic liquids (ILs) have emerged as the primary alternative solvents to hazardous organic solvents used in microextraction techniques because they are regarded as environmentally friendly (green) compounds. Ionic liquids are defined as salts with melting points below 100 °C and are composed of bulky organic cations, such as [alkylimidazolium], [pyridinium or alkylpyridinium], [*n*-hydroxyethylammonium], [alkylammonimum], [pyrrolidinium], and [alkylphosphonium], paired with various inorganic or organic anions, such as Cl^-, Br^-, I^-, BF_4^-, PF_6^-, NTF_2^-, CH_3COO^-, HSO_4^-, and $CH_3SO_3^-$.[4] The molecular structure of ionic liquids (ILs) enables them to interact with organic molecules and inorganic ions through various interactions, including electrostatic interactions, ion exchange, π–π stacking, and hydrogen bonding. Task-specific ionic liquids (TSILs), also referred to as functionalized ionic liquids (FILs), represent a subclass of ionic liquids characterized by their high selectivity toward a target analyte or a specific group of analytes. This unique property has made them highly valuable materials for sample preparation applications, where selectivity is a crucial factor, particularly in cases in which interfering species are present or when non-selective detection systems are employed. TSILs/FILs have been designed, synthesized, and applied in a wide range of specialized fields, including catalysis, electrochemistry, catalyst immobilization, reagent systems, supported phases, metal-ion separation/extraction, nanomaterial synthesis, and ion-conducting materials.[5,6] Both conventional room-temperature ionic liquids (RTILs) and TSILs/FILs have demonstrated considerable potential for the extraction of metal ions, including U(VI), Am(III), Co(II), Cd(II), Zn(II), and Ni(II), from aqueous media through the formation of stable metal complexes.[7] Several efforts have been made to incorporate various coordinating functional groups into the structure of ionic liquids, thereby enhancing their applicability for the separation and extraction of a wide range of analytes, particularly inorganic species. These modifications include the introduction of amine, hydroxyl, ethylamine, carboxylic acid, thiourea, ethylene glycol, macrocyclic ether, and 2-hydroxybenzylamine groups into ionic liquid structures, leading to the development of a variety of task-specific ionic liquids (TSILs).[8,9] It is important to design a series of TSILs for the selective extraction of metal ions from aqueous phases without the need for additional reagents such as ligands or complexing agents. Such extraction systems rely solely on task-specific ionic liquids as the extracting phase, without any auxiliary components. The use of external complexing agents in the extraction process increases the overall cost and reduces the industrial applicability of the method. One of the most important metal ions that must be determined at trace levels in various samples, particularly in different water sources, is chromium, as it exists in two stable oxidation states, Cr(III) and Cr(VI). Cr(III) is generally not toxic to humans, animals, or plants at normal concentrations; however, Cr(VI) is highly toxic even at trace levels. In contrast, Cr(VI) is strongly toxic and carcinogenic and is associated with various severe health hazards.[10] Cr(VI) is a strong oxidizing agent that can generate free radicals during its reduction to Cr(III). Cr(VI) is not naturally present in water and is primarily introduced through anthropogenic activities, mainly *via* industrial waste discharges.[11] Numerous reports have described the extraction of chromium from aqueous solutions or water samples using various extraction and microextraction techniques, such as synergistic extraction systems,[12] electromembrane extraction,[13] ultrasound-assisted extraction,[14] adsorption,[15] solvent extraction,[16] magnetic nanoparticles,[17] liquid–liquid extraction,[18] liquid-phase extraction,[19] solid-phase extraction,[20] micro-solid phase extraction,[21] emulsion liquid membranes,[22] low-pressure liquid oxidation,[23] dispersive liquid–liquid microextraction, *etc.*.[24] In all of the aforementioned methods, similar system components are typically required, particularly complexing agents and hazardous organic solvents. In contrast, in*in situ* solvent formation microextraction (ISFME), which is a variant of homogeneous liquid–liquid microextraction, an ionic liquid is employed, and no complexing agent is required when task-specific ionic liquids (TSILs) are used.[25] The *in situ* solvent formation microextraction (ISFME) technique was first introduced by several authors in 2009.[26] In this approach, ionic liquids (ILs) are used as the extractant or secondary phase and are initially completely dissolved in the aqueous phase because no interface or boundary exists between the aqueous and organic phases (*i.e.*, both phases are mutually miscible). As a result, the extraction process proceeds rapidly and efficiently. After the transfer of the analyte from the aqueous phase to the secondary phase, a counter ion is added to the system, inducing the conversion of the water-miscible ionic liquid into a water-immiscible form, thereby initiating phase separation. The main advantages of this technique include high extraction efficiency, simplicity, rapidity, and suitability for saline media.[27] ISFME is a simple, fast, cost-effective, and environmentally friendly technique that is compatible with high-salt-content samples and is widely applied in various extraction systems.[28] In the present study, the extraction and determination of Cr(III) and Cr(VI) ions in real water samples were performed using ISFME coupled with atomic absorption spectrometry (AAS).

In contrast to many previously reported selective chemical speciation methods for chromium species or metal ion extraction methods, which require additional complexing agents to transfer analytes from the aqueous phase to the secondary phase, no external complexing agent is required here because the task-specific ionic liquid acts simultaneously as both the complexing agent and the extractant phase. In the proposed method, following the formation of a hydrophilic Cr-[QPy][Br] complex in the aqueous phase and its preconcentration, ammonium hexafluorophosphate (NH_4PF_6) is added, resulting in the conversion of [QPy][Br] into a hydrophobic ionic liquid ([QPy][PF_6]) and the formation of a separate secondary phase. To optimize the extraction of chromium species, the effects of various parameters influencing the ISFME efficiency were evaluated and investigated. Here, for the first time, a combined analytical-modelling strategy was applied to selective chemical speciation of chromium species *via* ISFME, comprising the

following steps: (1) screening of experimental parameters and their domains using a two-level fractional factorial design; and (2) application of a central composite design within the response surface methodology framework to develop a predictive model describing the relationship between responses and significant variables. Finally, the optimized procedure was successfully applied for the microextraction and determination of Cr(III) and Cr(VI) ions in several real water and urine samples. In this study, chromium speciation is considered in an operational sense. The proposed method does not rely on chromatographic separation or redox transformation but instead exploits the differential chemical interactions of Cr(III) and Cr(VI) with the task-specific ionic liquid under controlled pH conditions. Therefore, the speciation described herein refers to selective extraction-based discrimination of chromium species.

Experimental

Chemicals and solutions

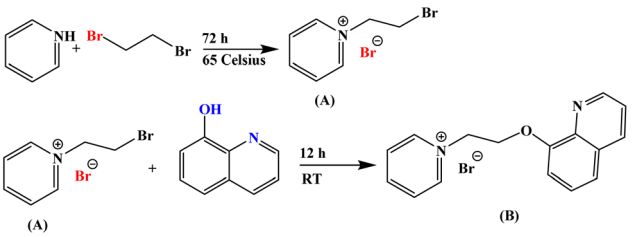
Analytical-grade reagents of the highest purity were used throughout the study, and all required solutions were prepared using doubly deionized distilled water. Pyridine, 1,2-dibromoethane, ammonium hexafluorophosphate, and 8-hydroxyquinoline were purchased from Merck (Darmstadt, Germany) and Sigma-Aldrich (St. Louis, MO, USA) and used for the synthesis of the task-specific ionic liquid 1-(2-(quinolin-8-yloxy)ethyl)pyridinium bromide. Chromium nitrate hexahydrate and potassium chromate were obtained from Merck (Darmstadt, Germany) and used for the preparation of stock solutions. Stock solutions of Cr(III) and Cr(VI) (1000 mg L^{-1}) were freshly prepared by dissolving appropriate amounts of chromium salts ($Cr(NO_3)_3 \cdot 6H_2O$ and K_2CrO_4) in doubly distilled water. Working standard solutions were prepared by appropriate dilution of the stock solutions. An acetic acid/sodium acetate buffer solution (0.1 mol L^{-1}), together with HCl and NaOH solutions (0.1 mol L^{-1}), was used for pH adjustment.

Preparation of chromium species solutions

Individual stock solutions of Cr(III) and Cr(VI) (1000 mg L^{-1}) were prepared separately from appropriate chromium salts using deionized water. For evaluation of the speciation capability of the proposed method, both individual chromium species and mixed solutions containing Cr(III) and Cr(VI) simultaneously were subjected to the extraction procedure under optimized conditions.

Instruments

The concentration of chromium ions in the aqueous phase was measured using a flame atomic absorption spectrometer (Varian SpectraAA-220, Australia). A chromium hollow cathode lamp was used as the radiation source and operated at a current of 10 mA. The absorbance of chromium was measured at a wavelength of 357.9 nm with a spectral slit width of 0.7 nm. pH measurements were performed using a digital pH meter equipped with a combination glass electrode (Metrohm 692 pH/ion meter, Switzerland).



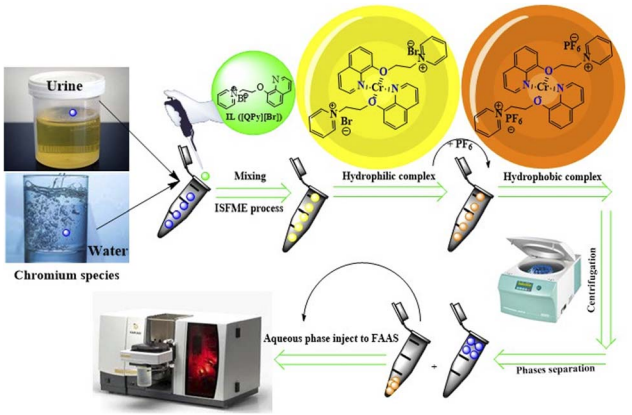
Scheme 1 Synthesis route of the pyridinuum-based task-specific ionic liquid 1-(2-(quinolin-8-yloxy)ethyl)pyridinium bromide.

Synthesis of the task-specific ionic liquid of 1-(2-(quinolin-8-yloxy)ethyl)pyridinium bromide ([QPy][Br])

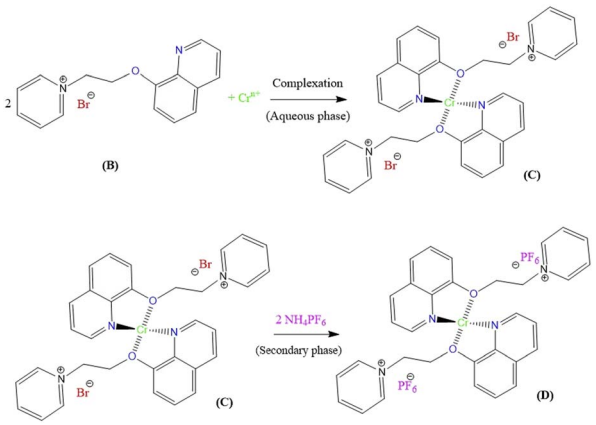
The synthesis steps for the task-specific ionic liquid 1-(2-(quinolin-8-yloxy)ethyl)pyridinium bromide (B) are schematically illustrated in Scheme 1. The general procedure, with minor variations particularly in the cation structure, is described as follows.[29] First, 3.46 mL (40 mmol) of 1,2-dibromoethane was added to 3.22 mL (40 mmol) of pyridine, and the mixture was stirred at 65 °C for 72 h to yield 10.67 g (31 mmol) of a white-yellow solid ionic liquid, 1-(2-bromoethyl)pyridinium bromide (A), with a yield of 77.5%. To remove impurities, including unreacted starting materials, product A was washed several times with acetone, and the residual solvent was subsequently removed at 70 °C for 2 h to obtain high-purity A. In the second step, equimolar amounts of 8-hydroxyquinoline (2.90 g, 20 mmol) and A (6.88 g, 20 mmol) were dissolved in ethanol, and the mixture was stirred under reflux for 12 h. The slightly yellow task-specific ionic liquid 1-(2-(quinolin-8-yloxy)ethyl)pyridinium bromide (B) was obtained after solvent evaporation followed by drying under vacuum.

In situ solvent formation microextraction (ISFME) procedure for selective determination and operational speciation of Cr(III) and Cr(VI)

A 10 mL aliquot of the sample solution containing 50 ng L^{-1} of Cr(III) and Cr(VI), together with an acetate buffer for pH



Scheme 2 *In situ* solvent formation microextraction (ISFME) procedure for the trace determination of chromium ions using a task-specific ionic liquid.



Scheme 3 Mechanism of *in situ* solvent formation microextraction (ISFME) for the extraction of chromium ions using the task-specific ionic liquid 1-(2-(quinolin-8-yloxy)ethyl)pyridinium bromide.

adjustment, was transferred into a 15 mL conical-bottom centrifuge tube. Subsequently, 200 mg (0.75 mmol) of 1-(2-(quinolin-8-yloxy)ethyl)pyridinium bromide (B), acting as a water-miscible (hydrophilic) functionalized ionic liquid, was added to the sample solution, and the mixture was shaken to initiate complex formation between chromium ions and B, leading to the formation of complex C (Schemes 2 and 3). After several minutes, 125 mg (0.75 mmol) of NH_4PF_6, serving as a counter ion, was added to the mixture containing complex C until microdroplets of the water-immiscible (hydrophobic) ionic liquid 1-(2-(quinolin-8-yloxy)ethyl)pyridinium hexafluorophosphate ([QPy][Br]) (D) were formed. Next, the mixture was centrifuged for 5 min at 4000 rpm to achieve phase separation and to quantify the extracted chromium ions. The fine droplets of phase D, containing the chelated chromium species, were isolated from the aqueous phase by centrifugation. Finally, the residual concentration of chromium remaining in the aqueous phase after phase separation was measured by flame atomic absorption spectrometry (FAAS), and the extraction efficiency was subsequently calculated from the difference between the initial and equilibrium concentrations. The extraction efficiency of chromium ions was calculated using eqn (1), where C_0 is the initial chromium ion concentration before extraction and C_{eq} is the equilibrium concentration of chromium ions after the extraction process, assuming that the total solution volume remains constant. Furthermore, the concentration factor (CF) of the procedure was calculated using eqn (2), where C_{sed} and V_{sed} represent the concentration of chromium ions in the sediment phase and the diluted volume of the sediment phase after dilution with ethanol prior to instrumental analysis, respectively. In the proposed ISFME procedure, chromium concentration after extraction was determined indirectly through measurement of the residual chromium concentration in the aqueous phase after phase separation by FAAS. Direct determination from the ionic liquid-rich sediment phase was avoided due to the high viscosity of the ionic liquid phase and instability during nebulization into the FAAS system. One the other hand, after phase separation, the aqueous phase (supernatant) was directly analyzed by FAAS for determination of the residual chromium concentration. The ionic liquid-rich phase was not introduced into the instrument due to its high viscosity and incompatibility with nebulization. In addition, the collected ionic liquid phase was diluted with ethanol (1 : 5, v/v) prior to FAAS analysis (concertation factor determination) to reduce viscosity and improve nebulization efficiency. In this work, chromium species were not transformed or separated by instrumental techniques; instead, their selective extraction behavior was used for operational speciation.

$$E\ (\%) = \frac{C_0 - C_{eq}}{C_0} \times 100 \quad (1)$$

$$CF = \frac{C_{sed}}{C_0} \quad (2)$$

Design of experiments (DOE)

Several parameters influence the extraction efficiency of chromium ions in the ISFME system. Therefore, a series of preliminary experiments were carried out to obtain useful information and a clearer understanding of the proposed ISFME speciation method. These preliminary experiments were performed under the conditions described in the procedure section. One set of experiments was conducted using solutions containing either Cr(III) or Cr(VI) at a concentration of 50 ng L^{-1}, and the results revealed that the task-specific ionic liquid exhibited a higher affinity for Cr(VI) compared to Cr(III). Therefore, using the synthesized task-specific ionic liquid, each chromium species could be selectively separated, and the extraction efficiency of one species did not significantly affect that of the other. Due to the significant influence of several parameters on chromium extraction in the ISFME system, including sample solution pH, the dosage of the hydrophilic task-specific ionic liquid, and the amount of ammonium hexafluorophosphate as a counter ion, these variables were selected to develop predictive models and optimize the extraction conditions. For this purpose, additional experiments were performed to identify the main influencing factors and to define their appropriate ranges for the Box–Behnken design. Then, accurate and reliable models for the extraction efficiencies of both chromium species were obtained. Three-dimensional (3D) response surface plots were generated to illustrate the interactions between variables and to identify the optimum conditions for maximum extraction efficiency. Furthermore, Design-Expert 8 (trial version) software was used to design the experiments and analyze the responses.

Real sample preparation

Several samples, including tap water (Borujerd, Lorestan, Iran), surface water (Fadak River, Borujerd, Lorestan), groundwater (collected from Ayatollah Boroujerdi University, Borujerd, Lorestan, Iran), and urine (male, 36 years old), were collected. The optimized ISFME procedure was applied for the determination of chromium ions in each real water and urine sample. Prior to analysis, all samples were filtered through a 0.45 μm cellulose membrane filter to remove suspended particulates. Finally, the

optimized procedure was applied to the real samples as described in the previous section. Prior to analysis, all samples were filtered through a 0.45 μm membrane filter. No digestion, oxidation, or reduction steps were applied to preserve the integrity of the selective chemical speciation of chromium species.

pH adjustment and buffering of sample solutions

All sample solutions were adjusted and maintained at the desired pH values using a 0.1 mol L^{-1} acetate buffer system prepared from acetic acid and sodium acetate. This buffer system was selected due to its effective buffering capacity within the studied pH range (5.0–6.0), ensuring stable and reproducible experimental conditions during the extraction process. For fine adjustment of pH values outside the buffering equilibrium or for precise setting of target pH levels, dilute hydrochloric acid (HCl, 0.1 mol L^{-1}) and sodium hydroxide (NaOH, 0.1 mol L^{-1}) solutions were used as required. The pH measurements were performed using a calibrated digital pH meter equipped with a combined glass electrode, and all measurements were carried out at room temperature. The use of the acetate buffer minimized pH fluctuations during the complexation and phase separation steps, thereby ensuring the reliability and repeatability of the microextraction procedure.

Results and discussion

Characterization of the synthesized task-specific ionic liquid 1-(2-(quinolin-8-yloxy)ethyl)pyridinium bromide ([QPy][Br])

The FTIR spectrum of [QPy][Br] is shown in Fig. 1. The absorption bands in the range of 481.17–990.79 cm^{-1} are attributed to the fingerprint region of the ionic liquid, which is characteristic of the molecular structure of the TSIL. The bands at 1002.36–1150.08 cm^{-1} correspond to the stretching vibrations of C–N and C–O bonds. The 1407.32–1478.31 cm^{-1} region is assigned to the aromatic C–C stretching vibrations (Ar C–C). The bands observed at 2852.59–3085.49 cm^{-1} are attributed to C–H stretching vibrations, indicating the presence of $-CH_2$ groups in the linker chain between the ionic liquid moieties. The broad band at 3425.59 cm^{-1} corresponds to O–H stretching vibrations, which are associated with adsorbed moisture in the TSIL structure. Overall, the FTIR results confirm the successful formation of [QPy][Br] and verify its key functional groups and bonding characteristics.

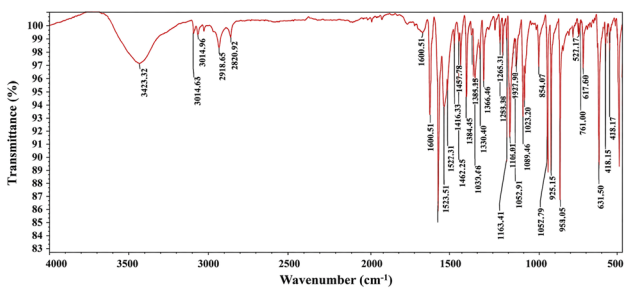


Fig. 1 FTIR of the ionic liquid 1-(2-(quinolin-8-yloxy)ethyl)pyridinium bromide.

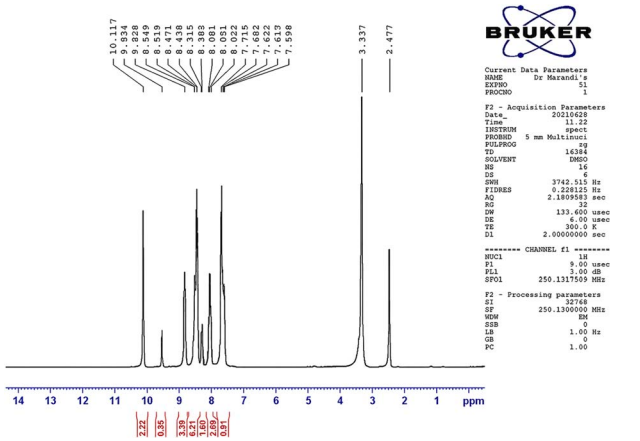


Fig. 2 ^{1}HNMR of the ionic liquid 1-(2-(quinolin-8-yloxy)ethyl)pyridinium bromide.

The ^{1}H NMR spectrum of [QPy][Br] is shown in Fig. 2. The signal at 3.337 ppm is attributed to the methylene ($-CH_2-$) protons in the linker chain. The signals in the range of 7.598–7.715 ppm correspond to the aromatic protons of the quinoline ring at different positions, while the signals observed at 8.022–8.828 ppm are assigned to the aromatic protons of the pyridine ring. Overall, the ^{1}H NMR results confirm the structure of the ionic liquid, although minor signals indicate the presence of trace impurities.

The successful synthesis of the task-specific ionic liquid 1-(2-(quinolin-8-yloxy)ethyl)pyridinium bromide was further confirmed by elemental analysis (CHN), oxygen content determination, and bromide quantification *via* the Volhard titration method. As summarized in Table 1, the experimentally obtained values are in excellent agreement with the theoretically calculated composition, indicating high purity and successful formation of the target ionic liquid. In particular, the close agreement between the experimental and theoretical percentages of carbon, hydrogen, nitrogen, oxygen, and bromine strongly supports the proposed molecular structure. The bromide counter-ion content determined by Volhard titration further confirms the correct incorporation of the anion in the final ionic liquid framework. It is worth noting that FTIR and ^{1}H NMR analyses of the starting materials were not performed in this study, as the reactants were commercially available and the synthetic route is well-established in the literature. However, the structural assignment of the product was carried out based on comprehensive spectroscopic characterization (FTIR and ^{1}H NMR) of the final compound together with elemental analysis and comparison with previously reported pyridinium-based ionic liquids. Overall, the combined analytical results provide strong and reliable evidence for the successful synthesis and structural integrity of the task-specific ionic liquid.

Design of experiments

The preliminary experiments indicated that sample solution pH, hydrophilic task-specific ionic liquid dosage, and ammonium hexafluorophosphate amount are the dominant factors

Table 1 Elemental analysis of the ionic liquid 1-(2-(quinolin-8-yloxy)ethyl)pyridinium bromide

	Measured (expected) (%)				
Target	C	H	N	O	Br
[QPy][Br]	57.80 (58.02)	4.50 (4.57)	8.35 (8.46)	4.87 (4.83)	23.50 (24.12)

affecting the extraction efficiencies of chromium ions. The formation of complexes between chromium ions and the ionic liquid, similar to conventional metal–ligand complexes, is strongly dependent on the pH of the aqueous phase. Therefore, the pH influences the extraction process through the protonation/deprotonation state of the functional groups (–O and –N) present in the task-specific ionic liquid. At acidic pH values, the protonated $-NH^+$ and $-OH^+$ groups of 8-hydroxyquinoline hinder effective chelation with Cr(III) and Cr(VI) species due to electrostatic repulsion. On the other hand, at basic pH values (pH > 7), precipitation of chromium species as $Cr(OH)_3$ and $Cr(OH)_6$ may occur. As a result, the optimum pH range for chromium extraction was found to be 5.0–6.0. Based on the results reported by Sadeghi *et al.*, a similar pH range of 4.0–6.0 was also reported for the extraction of Cr(VI), which is in good agreement with the present study.[30] Furthermore, temperature (25–50 °C) and extraction time (1–10 min) were found to be statistically insignificant parameters. To develop reliable and predictive models describing the relationship between experimental variables and extraction efficiencies of chromium ions, the Box–Behnken design (BBD) was employed for the three significant factors. The selected parameters were investigated at three levels: low (−1), center (0), and high (+1), as summarized in Table 2, while all other variables were kept constant.

The selection of the studied variables was based on preliminary univariate experiments which indicated that pH, ionic liquid dosage, and counter-ion amount were the most influential factors affecting extraction efficiency, while other variables such as temperature and extraction time showed negligible effects within the studied ranges. Therefore, these three factors were selected for further optimization using BBD. Although pH is chemically related to metal–ligand complex formation, in the statistical design it is treated as an independent variable from ionic liquid and counter-ion dosages, which mainly govern phase formation and separation behavior. The selected pH range (5.0–6.0) was chosen intentionally as a narrow but critical region where significant changes in complexation efficiency occur, based on preliminary studies. At lower pH values, protonation of donor atoms reduces coordination ability, while at higher pH values partial hydrolysis of chromium species may occur.

Table 2 The parameters, parameter labels, and their levels

		Levels		
Parameter	Label	−1	0	+1
Sample pH	*A*	5	5.5	6
Task-specific ionic liquid dosage	*B*	100	200	300
Counter-ion dosage	*C*	75	125	175

The selection of the number of experimental points (N) was carried out according to eqn (3):

$$N = 2k(k - 1) + C_p \quad (3)$$

In eqn (3), k represents the number of factors and C_p denotes the number of center points. In the present study, k and C_p were set to 3 and 5, respectively; therefore, seventeen experiments were designed. The experimental design was analyzed using statistical software. The results indicated that the most suitable predictive models were quadratic. Owing to the orthogonality of the design, non-significant terms were eliminated based on their significance levels to avoid model overfitting.[31] A significance level of 5% ($p < 0.05$) was applied in the present study. From the Box–Behnken design, the following quadratic polynomial equations (eqn (4) and (5)) were obtained for chromium extraction efficiencies, enabling the establishment of the relationship between the evaluated parameters and the responses. In the proposed equations, A represents the pH of the sample solution, B denotes the dosage of the task-specific ionic liquid (mg), and C corresponds to the dosage of ammonium hexafluorophosphate (mg).

$$\text{Extraction efficiency Cr(III)} = +68.18 + 7.14A + 10.12B + 5.13C - 6.21A^2 - 8.32B^2 - 9.31C^2 \quad (4)$$

$$\text{Extraction efficiency Cr(VI)} = +79.56 - 4.67A + 20.11B + 7.41C + 3.33BC - 7.34A^2 - 14.16B^2 - 12.59C^2 \quad (5)$$

The comparative, adjusted, and predicted R^2 values are presented in Table 2, along with the derived equations for chromium extraction efficiencies as responses. The coefficient of determination indicated that only 0.81% and 0.32% of the total variation were not explained by the models for Cr(III) and Cr(VI), respectively. The predicted R^2 values for Cr(III) and Cr(VI) were in good agreement with the adjusted R^2 values, indicating that no significant lack-of-fit or non-significant terms were present in the developed models.

The analysis of variance (ANOVA) was applied to the experimental data to estimate the standard errors of the coefficients, and the obtained results are summarized in Table 3. It was found that the linear coefficients (A, B, and C) as well as the quadratic terms (A^2, B^2, and C^2) were statistically significant for the extraction efficiencies of both chromium species. In addition, the

Table 3 Analysis of variance (ANOVA) for the Box–Behnken design

	Extraction efficiency for Cr^{3+}					Extraction efficiency for Cr^{6+}				
Parameter	Sum of square	Degree of freedom	Mean square	*F*-Value	*P*-Value	Sum of square	Degree of freedom	Mean square	*F*-value	*P*-value
Model	3982.12	9	429.11	76.34	<0.0001	5765.40	9	616.54	259.43	<0.0001
A	539.12	1	539.12	98.11	<0.0001	120.11	1	120.11	49.34	<0.0001
B	1812.22	1	1812.22	317.23	<0.0001	2896.21	1	2896.21	1234.22	<0.0001
C	360.32	1	360.32	66.54	<0.0001	500.29	1	500.29	213.56	<0.0001
AB	0.034	1	0.034	0.0038	0.9432	0.97	1	0.97	0.38	0.5123
AC	1.56	1	1.56	0.28	0.5430	0.73	1	0.73	0.32	0.5235
BC	19.11	1	19.11	3.11	0.1215	20.54	1	20.54	9.19	0.0187
A^2	218.98	1	218.98	40.32	0.0004	286.39	1	286.39	125.67	<0.0001
B^2	391.10	1	391.01	67.80	<0.0001	983.92	1	983.92	427.37	<0.0001
C^2	488.23	1	488.23	84.21	<0.0001	558.93	1	558.93	237.57	<0.0001
Residual	37.56	7	5.37			15.34	7	2.14		
Lack of fit	29.49	3	9.20	3.50	0.1320	8.92	3	2.54	1.34	0.3624
Pure error	11.40	4	2.45			7.84	4	2.01		
Cor total	3887.56	16				5776.93	16			

Model statics	Extraction efficiency for Cr^{3+}	Extraction efficiency for Cr^{6+}
R^2	0.9911	0.9982
R^2 adjusted	0.9861	0.9969
R^2 predicted	0.9611	0.9771

ANOVA results indicated that the interaction term *BC* was also significant in the model for Cr(VI) extraction efficiency. The *F*-values of 76.34 and 259.43 for Cr(III) and Cr(VI), respectively, demonstrated that both models were statistically significant. The lack-of-fit *p*-values were not significant relative to the pure error, indicating that the models fit the experimental data well. Another criterion for evaluating model adequacy is the normal probability plot of standardized residuals. The data points in this plot lie reasonably close to a straight line, confirming that the residuals are normally distributed with a mean of zero and a constant (but unknown) variance, in agreement with the assumptions of the analysis. As shown in Fig. 3(a–f), three response surface plots were generated for each chromium species to graphically illustrate the relationship between the three main variables and the response. These plots were used to determine the optimum conditions for achieving maximum extraction efficiency for both chromium species. From Fig. 3(a, b, d, and e), it is evident that increasing the sample pH enhances the extraction efficiency of both Cr(III) and Cr(VI), with maximum extraction achieved at pH values above 5 for Cr(III). However, the optimum pH was determined to be 5.5, and this value was selected to maximize the extraction efficiency of both species simultaneously. In addition, increasing the task-specific ionic liquid dosage significantly improved the extraction efficiency of both chromium species, due to the enhanced formation of metal–ionic liquid complexes. Above 200 mg of ionic liquid, the extraction efficiencies reached a maximum. Furthermore, the dosage of ammonium hexafluorophosphate is a crucial parameter for phase separation, as it induces the conversion of the hydrophilic ionic liquid into a hydrophobic phase. As shown in Fig. 3(b, c, e, and f), the extraction efficiencies of both chromium species increased with increasing ammonium hexafluorophosphate dosage; therefore, 125 mg was selected as the optimum value. At lower amounts of this counter ion, complete phase separation was not achieved, since the ionic liquid retains partial hydrophilicity under these conditions.

According to the results presented in Fig. 3, the optimum conditions required to achieve maximum extraction efficiencies for chromium ions were a sample solution pH of 5.5, a task-specific ionic liquid dosage of 200 mg, and an ammonium hexafluorophosphate dosage of 125 mg. The other investigated parameters, including sample solution temperature, centrifugation time, and centrifugation rate, which showed no significant effect on the extraction procedure, were maintained at fixed values of 25 °C, 1 min, and 4000 rpm, respectively. Under the optimized conditions, quantitative extraction efficiencies of 101.6% and 100.5% were obtained for Cr(III) and Cr(VI), respectively. The predicted optimum extraction efficiencies at a 95% confidence level were 101.2% and 100.8% for Cr(III) and Cr(VI), respectively. The adequacy of the developed models was evaluated using statistical plots comparing the experimentally obtained extraction efficiencies with the values predicted by the models. The results demonstrated good agreement between the predicted and experimental responses, confirming the reliability and suitability of the proposed models.

Selective chemical speciation of chromium species performance

To investigate the chromium species-dependent extraction behavior of the proposed ionic liquid-based microextraction

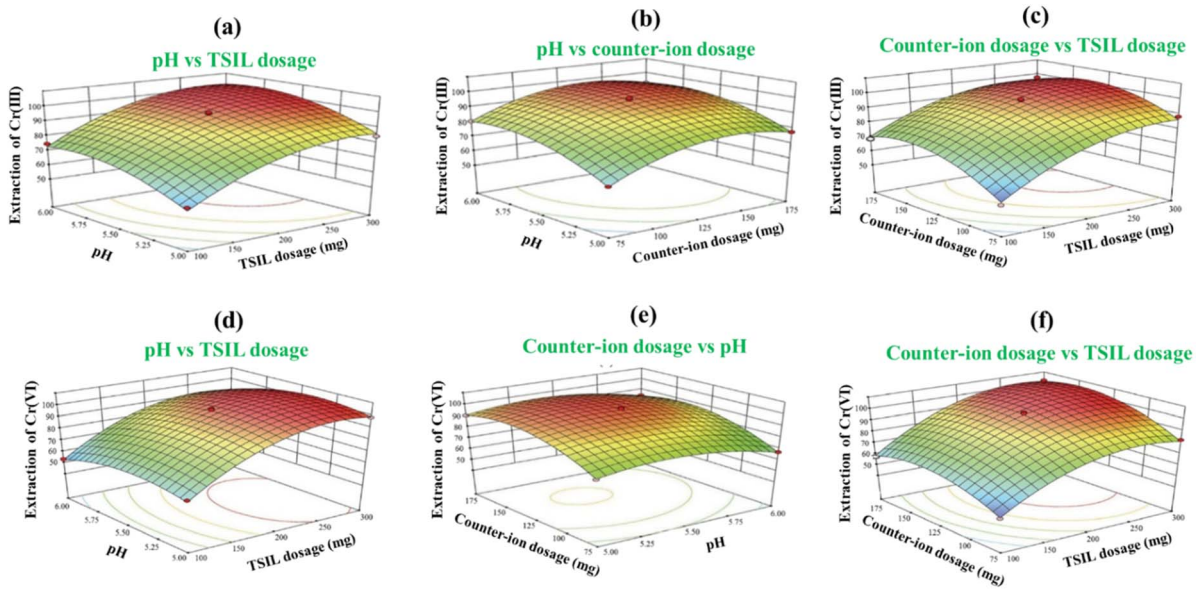


Fig. 3 Three-dimensional (3D) response surface plots showing (a) the extraction percentage of Cr(III) as a function of sample solution pH (*A*) and TSIL dosage (*B*); (b) the extraction percentage of Cr(III) as a function of sample solution pH (*A*) and counter-ion amount (*C*); (c) the extraction percentage of Cr(III) as a function of TSIL dosage (*B*) and counter-ion amount (*C*); (d) the extraction percentage of Cr(VI) as a function of sample solution pH (*A*) and TSIL dosage (*B*); (e) the extraction percentage of Cr(VI) as a function of sample solution pH (*A*) and counter-ion amount (*C*); and (f) the extraction percentage of Cr(VI) as a function of TSIL dosage (*B*) and counter-ion amount (*C*).

Table 4 Operational speciation behaviour of the proposed method for selective extraction of Cr(III) in the presence of Cr(VI)

Sample	Added Cr(III), ng L^{-1}	Added Cr(VI), ng L^{-1}	Measured Cr(VI), ng L^{-1}	Recovery Cr(III)
Mixed solution 1	50	50	48.9	97.8
Mixed solution 2	100	100	98.6	98.6
Mixed solution 3	50	50	49.1	98.2
Mixed solution 4	100	100	10.2	101.2

system, extraction experiments were performed using both individual chromium species and mixed solutions containing Cr(III) and Cr(VI) simultaneously under the optimized conditions (Table 4). The results indicated a clear difference in the extraction behavior of the two chromium species. Cr(III) was preferentially extracted due to its cationic nature and its stronger coordination affinity toward the donor atoms (N and O) of the functionalized ionic liquid. In contrast, Cr(VI), which predominantly exists as oxyanionic species in aqueous media, exhibited significantly weaker interaction with the extraction phase and therefore largely remained in the aqueous solution under the studied conditions. The recovery results obtained from mixed-species experiments further confirmed that the presence of Cr(VI) does not adversely affect the extraction efficiency and determination of Cr(III). Overall, these findings indicate that the proposed method enables selective discrimination of chromium species based on their different chemical interaction behaviors within the ISFME system, demonstrating its suitability for operational speciation and selective determination of chromium species in complex matrices. The selective chemical discrimination between chromium species is achieved in a single-step extraction system. Selectivity arises from the pH-dependent formation of cationic Cr(III) complexes, which strongly interact with the oxygen and nitrogen donor sites of the TSIL, while Cr(VI) remains predominantly as anionic chromate species with significantly weaker interaction, leading to differential extraction efficiencies.

Robustness of the ISFME technique in the presence of high salt concentrations

It is noteworthy that one of the unique advantages of the ISFME method over other microextraction techniques is its compatibility with the extraction of analytes from samples containing high salt concentrations.[25] Based on the salting-out effect, the addition of salts may enhance the extraction efficiency of metal ions in ISFME and other microextraction procedures. However, when ionic liquids are used as the extraction solvent (secondary phase), phase separation in ISFME and related liquid–liquid microextraction methods may be inhibited at high salt concentrations due to increased solubility of the ionic liquid. This phenomenon occurs through ion-exchange processes

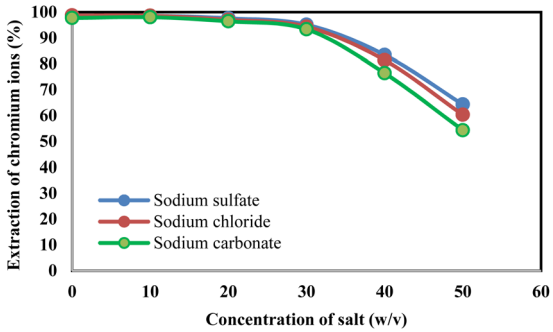


Fig. 4 Effect of various salt concentrations on the extraction efficiencies of chromium ions under the optimum conditions.

between the ionic liquid anion and salt anions.[2] Therefore, evaluating the robustness of the ISFME method in the presence of high salt concentrations is important, as it represents one of the key advantages of this technique. Accordingly, the effects of salt type and concentration on the ISFME performance for chromium extraction were investigated. The microextraction experiments were carried out under optimized conditions in the presence of different concentrations (5–50%, w/v) of soluble salts, including sodium sulfate, sodium chloride, and sodium carbonate.

As shown in Fig. 4, the extraction efficiencies of chromium ions remained nearly constant with increasing salt concentration up to 25% (w/v). The decrease in extraction efficiency at higher salt concentrations (>25%, w/v) can be attributed to the exchange of the PF_6^- anion of the ionic liquid with competing salt anions, resulting in the conversion of the hydrophobic ionic liquid into a more hydrophilic form. Consequently, effective phase separation at the end of the extraction process no longer occurs. Therefore, the proposed ISFME procedure demonstrates high tolerance toward saline matrices, with negligible effects on extraction efficiency at salt concentrations of up to 25% (w/v).

Effects of interfering ions on chromium microextraction

Evaluation of the effects of common coexisting ions on the extraction efficiency of chromium species is essential for assessing the selectivity of the proposed microextraction method. The microextraction procedure was performed under the optimized conditions using solutions containing 50 ng L^{-1} of chromium ions in the presence of various concentrations of potential interfering ions. The tolerance limit was defined as the maximum interferent-to-analyte ratio that produced a relative error of less than 5% in the extraction efficiency of each chromium species. The results presented in Table 3 indicate that alkali and alkaline earth metal ions did not significantly interfere with the extraction of chromium ions. Furthermore, most transition metal ions showed no serious interference effects on chromium extraction, except for Zn^{2+}, Pb^{2+}, and Cd^{2+} ions. In addition to metal cations, the effects of several common anions, including F^-, Cl^-, Br^-, I^-, NO_3^-, and HCO_3^-, were also investigated, and no significant interference in chromium extraction was observed. As shown in Table 5, the high selectivity of the synthesized task-specific ionic liquid toward chromium ions over other transition metal ions resulted in high extraction efficiencies ranging from 97.0% to 100.1%. Therefore, the satisfactory selectivity of this extraction system enables the proposed ISFME method to be effectively applied for the determination of chromium ions in real samples with complex matrices.

Analytical properties of the ISFME

To validate the proposed ISFME procedure and evaluate the analytical figures of merit, the optimized speciation conditions

Table 6 Determination of various chromium species in environmental samples[a]

	Added (ng L^{-1})		Measured (ng L^{-1})		Recovery (%)	
Sample	Cr^{3+}	Cr^{6+}	Cr^{3+}	Cr^{6+}	Cr^{3+}	Cr^{6+}
Tap water	0	0	ND	ND	—	—
	50	50	52.5	47.3	105.0	94.6
	100	100	105.0	98.1	105.0	98.1
Surface water	0	0	25.7	ND	—	—
	50	50	73.5	48.4	97.0	96.8
	100	100	128.4	98.2	102.1	98.2
Ground water	0	0	ND	ND	—	—
	50	50	48.6	47.9	97.2	95.8
	100	100	100.5	97.2	100.5	97.2
Urine	0	0	ND	ND	—	—
	50	50	47.5	47.0	95.0	94.0
	100	100	96.7	97.0	96.7	97.0

[a] ND = Not detected, each experiment was repeated 7 times under optimum conditions.

Table 5 The effect of interfering agents on the extraction efficiencies of chromium ions

Tolerance limit (w/w)	Interferer	Extraction of Cr(III), %	Extraction of Cr(VI), %
16 000	Na^+, K^+, Li^+, Ba^{2+}, Ca^{2+}, F^-, Cl, Br^-, I^-, NO_3^- and HCO_3^-	97.8–99.8	96.8–100.1
500	Mn^{2+}, Hg^{2+}, and Sn^{2+}	97.9–98.2	96.5–99.5
400	Fe^{3+}, Cu^{2+}, Co^{2+}, and Mg^{2+}	97.8–98.9	98.8–97.7
300	Al^{3+} and Ni^{2+}	97.5–98.5	98.1–100.0
100	Pb^{2+}, Cd^{2+}, and Zn^{2+}	97.4–98.2	97.0–97.8

Table 7 Comparison of the characteristics of the present ISFME method with several extraction/microextraction methods for operational speciation behavior and determination of chromium species

	LOD[a] (ng L^{-1})		LDR[b] (ng L^{-1})		RSD[c] (%)			
Method	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	CF[d]	Ref.
DLLME[e]	3.7	2.1	20–200	70–250	9.07	2.4	43	24
TCDLLME[f]	5.4	2.4	50–200	25–150	3.05	4.2	42	30
USAEME[g]	14.8	14.8	30–400	30–400	3.8	3.8	250	32
DLLME	2.0	2.0	5–200	5–200	8.0	8.0	240	33
SALLME[h]	—	1250	—	3000–150000	—	1.5	100	34
DLLME	1000	400	3–800	5–200	3.3	4.0	16.7	35
ISFME	20.6	4.8	100–500	10–1000	3.1	2.6	85	This work

[a] Limit of detection. [b] Linear dynamic range. [c] Relative standard deviation. [d] Concentration factor. [e] Dispersive liquid–liquid microextraction. [f] Temperature-controlled dispersive liquid–liquid microextraction. [g] Ultrasound-assisted emulsification-microextraction. [h] Salt-assisted liquid–liquid microextraction.

were applied. The calibration curves exhibited good linearity within the ranges of 100–500 ng L^{-1} for Cr(III) and 10–1000 ng L^{-1} for Cr(VI), with correlation coefficients (R^2) higher than 0.98. The limits of detection (LOD = $3S_b/m$), defined as three times the standard deviation of the blank signal (S_b) divided by the slope of the calibration curve (m), were 20.6 and 4.8 ng L^{-1} for Cr(III) and Cr(VI), respectively. The limits of quantification (LOQ = $10S_b/m$) were calculated to be 68.0 and 15.8 ng L^{-1} for Cr(III) and Cr(VI), respectively. The inter-day precision of the proposed ISFME speciation method, expressed as relative standard deviation (RSD%), was evaluated by performing six independent extraction experiments at a chromium concentration of 50 ng L^{-1} under the optimized conditions. The RSD values were 3.1% and 2.6% for Cr(III) and Cr(VI), respectively, confirming the satisfactory precision of the method. The concentration factor (CF), calculated using eqn (2), was found to be 85 for both chromium species.

Analysis of environmental samples

To evaluate the accuracy of the method and to investigate matrix effects on the extraction of chromium species, the applicability of the proposed method was examined using several real samples, including tap water (Borujerd city tap water, Iran), surface water (Fadak River, Borujerd city, Iran), groundwater (groundwater from Ayatollah Boroujerdi University, Borujerd city, Iran), and a urine sample (from a healthy 36-year-old male), according to the proposed selective chemical speciation of chromium procedure. The obtained results showed that the concentrations of Cr(III) and Cr(VI) were close to the method's limits of detection and were not detected in some of the analyzed water and urine samples; therefore, the samples were spiked with standard solutions at 50 and 100 ng L^{-1}. The detailed results and recovery values are presented in Table 6. The recovery values for Cr(III) and Cr(VI) were in the ranges of 95.0–105.0% and 94.0–98.2%, respectively, indicating that the proposed ISFME method is suitable for the determination of these ions in various environmental samples. It is noteworthy that relatively higher levels of Cr(III) were observed in surface water, which may be attributed to anthropogenic inputs, such as the discharge of human waste into the water system. Furthermore, slightly lower recoveries for both chromium species in urine (<97%) can be attributed to its complex matrix composition, where the presence of various interfering ions may partially suppress the extraction efficiency of chromium species.

Comparison of the ISFME method with other chromium determination methods

The proposed ISFME method was compared with other reported extraction and microextraction methods used for the determination of chromium ions at trace levels, and the results are summarized in Table 7.[24,30,32–35] The ISFME method is comparable to the reported methods in terms of low detection limits, good precision, a wide linear dynamic range, and satisfactory concentration factors. It is noteworthy that, unlike most previously reported microextraction systems, which require the use of an additional complexing agent for chromium extraction, the present method operates as a complexing-agent-free system, leading to excellent analytical performance. From an industrial perspective, a complexing-agent-free system is highly advantageous, as it reduces reagent consumption and overall operational costs.

Conclusions

In the present study, an ISFME procedure coupled with flame atomic absorption spectrometry (FAAS) as a conventional analytical detection technique was successfully applied for the sensitive microextraction and speciation of chromium ions in water and urine samples, providing satisfactory detection limits, linear dynamic ranges, concentration factors, and precision. In this ISFME approach, a complexing-agent-free extraction system was employed. The task-specific ionic liquid [QPy][Br] was first successfully synthesized and characterized, and subsequently used as both the secondary phase and complexing agent for the extraction of chromium ions from aqueous media. In addition, a highly efficient optimization strategy based on statistical methodology was developed and

demonstrated to be effective and reliable for identifying statistically significant factors and optimizing their corresponding levels. Under optimal conditions, quantitative extraction efficiencies of 101.6% and 100.5% were obtained for Cr(III) and Cr(VI), respectively. Compared with other chromium determination methods, the proposed ISFME method offers several advantages, including stability in saline matrices, simplicity of operation, ease of use, the absence of additional complexing agents, and the use of environmentally friendly ionic liquids. In addition, the proposed extraction system successfully demonstrated selective extraction and operational speciation capability toward Cr(III) in the presence of Cr(VI), confirming its applicability for selective chemical speciation analysis of chromium in complex environmental samples. It should be emphasized that the term speciation in this work refers to an operational chemical approach based on selective extraction rather than instrumental species separation.

Informed consent statement

Written informed consent was obtained from all participants before sample collection and analysis. They were fully informed about the study's purpose, procedures, potential risks, and benefits. All individuals voluntarily agreed to provide their urine samples for research purposes. The study was conducted in strict accordance with ethical guidelines, ensuring the confidentiality and anonymity of all personal information. Additionally, participants retained the right to withdraw from the study at any stage without any consequence.

Author contributions

Salma Salmasi: formal analyses, methodology, investigation. Mehdi Hosseini: writing – review and editing, writing – original draft, visualization, validation, methodology, investigation, data curation, conceptualization. Ebaa Adnan Azooz: writing – review and editing, data curation, investigation.

Conflicts of interest

There are no conflicts to declare.

Data availability

Data will be made available on request.

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