Methods and objects of chemical analysis, 2024, Vol. 19, No. 3, 160–166

Cloud Point Extraction Method for Separation and Pre-concentration of Molybdenum and Zirconium Using Mixture of Surfactants from Natural Waters and their Determination by Spectrophotometry

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Received: April 22, 2024; Accepted: July 15, 2024
DOI: 10.17721/moca.2024.160-166

A simple and environmentally friendly technique, cloud point extraction (CPE), has been developed to analyse Molybdenum (Mo(VI)) and Zirconium (Zr(IV)) in water samples using spectrophotometry. This method involves the use of a surfactant mixture composed of Triton X-114 (TX-114) and cetyltrimethylammonium bromide (CTAB). In this approach, Mo(VI) and Zr(IV) metal ions are complexed with Pyrogallol red (PR) and Chrome Azurol S (CAS), respectively. The metal complexes of Mo(VI) and Zr(IV) are heated to reach the cloud point temperature and extracted into the micellar phase. Several parameters, such as pH, ligand concentrations, surfactant concentrations (TX-114 & CTAB), equilibration temperature, and equilibration time, were optimized to enhance the efficiency of the extraction process. Using the optimized conditions, linear calibration graphs were established over the concentration ranges of 1.23 - 37.0 μg L^{-1} for Mo(VI) and 8.05 - 112.78 μg L^{-1} for Zr(IV). The detection limits for Mo(VI) and Zr(IV) were determined to be 1.24 ng mL^{-1} and 9.92 ng mL^{-1}, respectively. The applicability of this method was successfully demonstrated in the analysis of Mo(VI) and Zr(IV) concentrations in river water and coastal waters, with recovery rates falling within the range of 87% to 101%.

Keywords: cloud point extraction, mixed micelles, Mo(VI), Zr(IV), pyrogallol red (PR), chrome azurol S (CAS)

Introduction

Metals such as Molybdenum (Mo(VI)) and Zirconium (Zr(IV)) can become toxic to humans when found in high concentrations [1, 2]. Molybdenum is an essential trace element required by plants, animals, and humans in very small amounts, serving as a cofactor for several enzymes involved in important metabolic processes. However, molybdenum can become toxic at elevated concentrations. In wastewater, the extent of its toxicity depends on its chemical form and oxidation state [3].

Zr(IV) serves various industrial purposes, including its use in the nuclear industry as a catalyst in organic reactions, textiles, metal alloys, dye pigments, and ceramics [4]. Both molybdenum (Mo(VI)) and zirconium (Zr(IV)) can potentially exhibit toxic properties in certain conditions, especially at higher concentrations in wastewater. Detecting these metals in the environment is challenging due to their low concentrations and interference from other substances. Therefore, it is essential to eliminate background effects before applying pre-concentration techniques like dispersive liquid-liquid microextraction [5], solid-phase extraction [6,7], solvent extraction [8], and cloud point extraction. Among these techniques, cloud point extraction stands out as it enables the preconcentration of both organic and inorganic compounds from different chemical systems. cloud point extraction of metals is a valuable and efficient technique for the separation and preconcentration of metal ions from aqueous solutions. Its successful application depends on factors such as the choice of surfactant, pH conditions, temperature, and the nature of the metal ions. Notably, cloud point extraction aligns with green chemistry principles as it avoids the use of harmful organic solvents while achieving higher analyte concentration compared to liquid-liquid extraction [9].

In cloud point extraction, a mixture of surfactants is often employed, combining an ionic surfactant (either cationic or anionic) with a non-ionic surfactant [10]. The non-ionic surfactant enhances hydrophobic interactions with the metal complex, while the ionic surfactant simplifies extraction through electrostatic interactions. The combination of cationic and non-ionic surfactants has been previously utilized for extracting organic compounds [11,12], dyes [13,14],

and metal ions [15]. This study presents the outcomes of employing mixed micelles of CTAB and TX-114 for cloud point extraction, followed by spectrophotometric analysis to quantify Mo(VI) and Zr(IV). Subsequently, this optimized approach was applied to determine the concentrations of Mo(VI) and Zr(IV) in diverse water samples.

Material and methods

Reagents, Solutions and Instruments

All chemicals utilized in this study were of analytical grade. CTAB, Triton TX-114, PR, and CAS were procured from Sigma-Aldrich, USA. Stock solutions of CTAB and TX-114 were prepared using doubly distilled water. To prepare the stock standard solutions for Mo(VI) and Zr(IV), precise quantities of ammonium heptamolybdatetetrahydrate from Merck (India) and the zirconyl oxychloride octahydrate from Sigma-Aldrich (USA) were dissolved, and the quantification of metal complexes was conducted using a UV-Vis spectrophotometer (UV-1800, Shimadzu).

CPE procedure for extraction of Mo(VI): In a 15 mL graduated test tube, acetate buffer at pH 4.6 and different concentrations of Mo(VI) (1.23–37.0 μg mL^{-1}) were added. This was followed by the addition of $1.2 \cdot 10^{-5}$ mol L^{-1} of ALS, 0.07 mL of 10% (w/v) CTAB, 1.6 mL of 10% (w/v) TX–114, and 0.6 mL of 30% (w/v) NaCl. The solution was then made up of 10.0 mL of double-distilled water and heated up to 353 K for 20 minutes in a thermostatic bath. The separation of two phases (bulk aqueous phase and coacervate phase (surfactant-rich phase)) was achieved by centrifugation for 5 min at 1500 rpm. The volume of the Coacervate phase is 0.75 mL. The whole system was cooled in an ice bath for 15 minutes to improve the viscosity of the coacervate phase and decanted the bulk aqueous phase. The coacervate phase was dissolved in 20% methanol and the spectrophotometric analysis was carried out at a wavelength of 608 nm.

CPE procedure for extraction of Zr(IV): In a 15 mL graduated test tube, acetate buffer at pH 4.2 and different concentrations of Zr(IV) (8.05–112.78 μg mL^{-1}) were added. This was followed by the addition of $0.3 \cdot 10^{-3}$ mol L^{-1} of CAS, 2.0 mL of 10% (w/v) TX–114, 0.5 mL of 10% (w/v) CTAB, and 0.8 mL of 30% (w/v) Na_2SO_4. The solution was then made up to 10.0 mL double distilled water and heated up to 323 K for 20 minutes in a thermostatic bath. The separation of two phases (bulk aqueous phase and coacervate phase (surfactant-rich phase)) was achieved by centrifugation for 10 min at 1000 rpm. The whole system was cooled in an ice bath for 15 minutes to improve the viscosity of the coacervate phase and decanted the bulk aqueous phase. The Obtained volume of the Coacervate Phase is 0.8 mL. The coacervate phase was dissolved in 20% methanol and the spectrophotometric analysis was carried out at a wavelength of 546 nm.

Results and discussion

The following reagents and reaction conditions were optimized, each one at a time.

Optimization of pH

The efficiency of extraction depends on the pH conditions during complex formation. We carried out the effect of pH on the formation of complexes and the extraction process for Mo(VI) and Zr(IV) within the pH range of 1.0 to 8.0. The most favorable recovery outcomes were achieved using an acetate buffer (CH_3COONa/CH_3COOH) within the pH range of 3.8 to 6.0 for both metal ions. Optimal recoveries were observed at pH 4.6 for Mo(VI) and 4.2 for Zr(IV) beyond which recovery rates decreased due to reduced hydrophobicity of the complexes (Figure 1a and Figure 2a). Consequently, pH 4.6 and 4.2 were selected as the optimum conditions for determining Mo(VI) and Zr(IV), respectively, in subsequent experiments.

Variation of the concentration of ligands

The ligand PR was selected for forming complexes with the Mo(VI) ion. Recovery of Mo(VI) was investigated across a concentration range of PR from $(0.48\text{-}4.80) \cdot 10^{-5}$ mol L^{-1}. With an increase in PR concentration, recoveries exhibited an upward trend until reaching $1.2 \cdot 10^{-5}$ mol L^{-1}, after which they stabilized. Consequently, a concentration of $1.2 \cdot 10^{-5}$ mol L^{-1} for PR was adopted for subsequent experiments (Figure 1b).

The ligand CAS was employed as a complexing agent for the Zr(IV) ion. CAS concentration was explored within the range of $(0.05\text{-}1.0) \cdot 10^{-3}$ mol L^{-1}. Extraction efficiency is relative to CAS concentration is depicted in Figure 2a. Percentage recovery displayed rapid improvement as CAS concentration increased from $0.05 \cdot 10^{-3}$ to $0.3 \cdot 10^{-3}$ mol L^{-1}, followed by a decline. Consequently, a concentration of $0.3 \cdot 10^{-3}$ mol L^{-1} for CAS was selected for subsequent experiments (Figure 2b).

Variation of the concentration of TX-114

The choice of the non-ionic surfactant TX-114 was based on its advantages, including a low cloud point temperature, cost-effectiveness, and reduced toxicity. The concentration of TX-114 varied from 0.4% (w/v) to 4.0% (w/v), revealing that lower concentrations resulted in diminished recoveries due to incomplete and inadequate extraction of the Mo(VI) and Zr(IV) metal complexes. Recovery rates improved with higher TX-114 concentrations, reaching their peak at 1.6% (w/v) and 2.0% (w/v) for Mo(VI) and Zr(IV), respectively (Figure 1c and Figure 2c).

Optimization of the concentration of CTAB

The analytes Mo(VI) and Zr(IV) ions, which have positive charges, engage with ligands PR and CAS, respectively, resulting in the formation of negatively charged complexes. Therefore, to ensure the complete extraction of these analytes, neutralization with positively charged species is necessary. Consequently, the cationic surfactant CTAB was

employed in conjunction with TX-114. The optimal CTAB concentration was determined across the range of 0.0% to 2.0% (w/v). The most favorable recovery rates were achieved at 0.07% w/v (for Mo(VI)) and 0.5% w/v (for Zr(IV)) (Figure 1d and Figure 2d).

Optimization of salt

Optimal cloud point temperatures around room temperature are convenient for extraction purposes. Since the TX-114 and CTAB mixture exhibits a cloud point temperature of approximately 363-373 K, the inclusion of a salting-out agent is a common practice to lower this temperature. In this study, NaCl and Na_2SO_4 were employed as salting-out agents, and their impact on extraction efficiency was assessed. The highest recovery for the Mo(VI) ion was observed at a concentration of 1.8% w/v NaCl. For Zr(IV), recovery rates increased until reaching a concentration of 2.4% w/v Na_2SO_4, beyond which a decreasing trend was observed.

Optimization of equilibration temperature and time

Optimizing equilibration time and temperature is crucial to achieve a method that offers both efficiency and practicality, including a brief equilibration period and proximity to room temperature. In this investigation, the equilibration temperature was explored within the range of 25-100 °C, while equilibration time was assessed over 5-60 minutes. The optimal conditions were determined to be 80°C for Mo(VI) and 50°C for Zr(IV) regarding temperature. Likewise, an equilibration time of 20 minutes was identified as ideal for both Mo(VI) and Zr(IV).

Analytical figures of merit

Utilizing the optimized conditions, calibration curves were constructed for Mo(VI) (Figure 3a) and Zr(IV) (Figure 3b). The linear ranges for Mo(VI) and Zr(IV) were determined as 1.23 – 37.0 μg mL^{-1} and 8.05 – 112.78 μg mL^{-1}, respectively. Strong correlation coefficients of 0.988 and 0.987 were achieved for Mo(VI) and Zr(IV), respectively. Notably, the limits of detection were found to be 1.24 ng mL^{-1} for Mo(VI) and 9.92 ng mL^{-1} for Zr(IV).

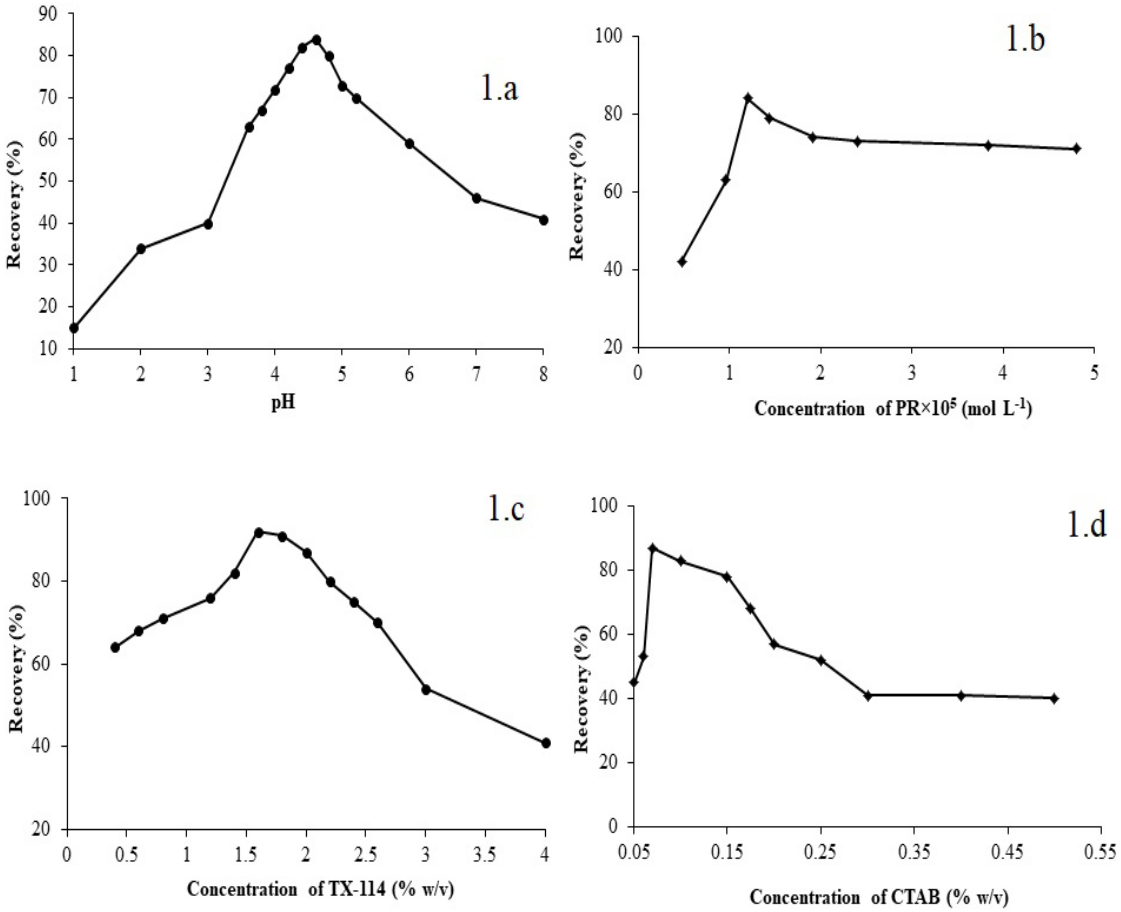

Figure 1. (a) Optimization of concentration of pH on recovery of Mo(VI), (b) Optimization of concentration of PR recovery of Mo(VI), (c) Optimization of concentration of TX-114 recovery of Mo(VI), (d) Optimization of concentration of CTAB recovery of Mo(VI). (Experimental conditions: pH = 4.6; [Mo(VI)] = 24.7 μg mL^{-1}; [PR] = $1.2 \cdot 10^{-5}$ mol L^{-1}; [TX-114] = 1.6 % w/v; [CTAB] = 0.07 % w/v; [NaCl] = 1.8 % w/v; Equilibration temperature = 80 ^{0}C; Equilibration time = 20 min.

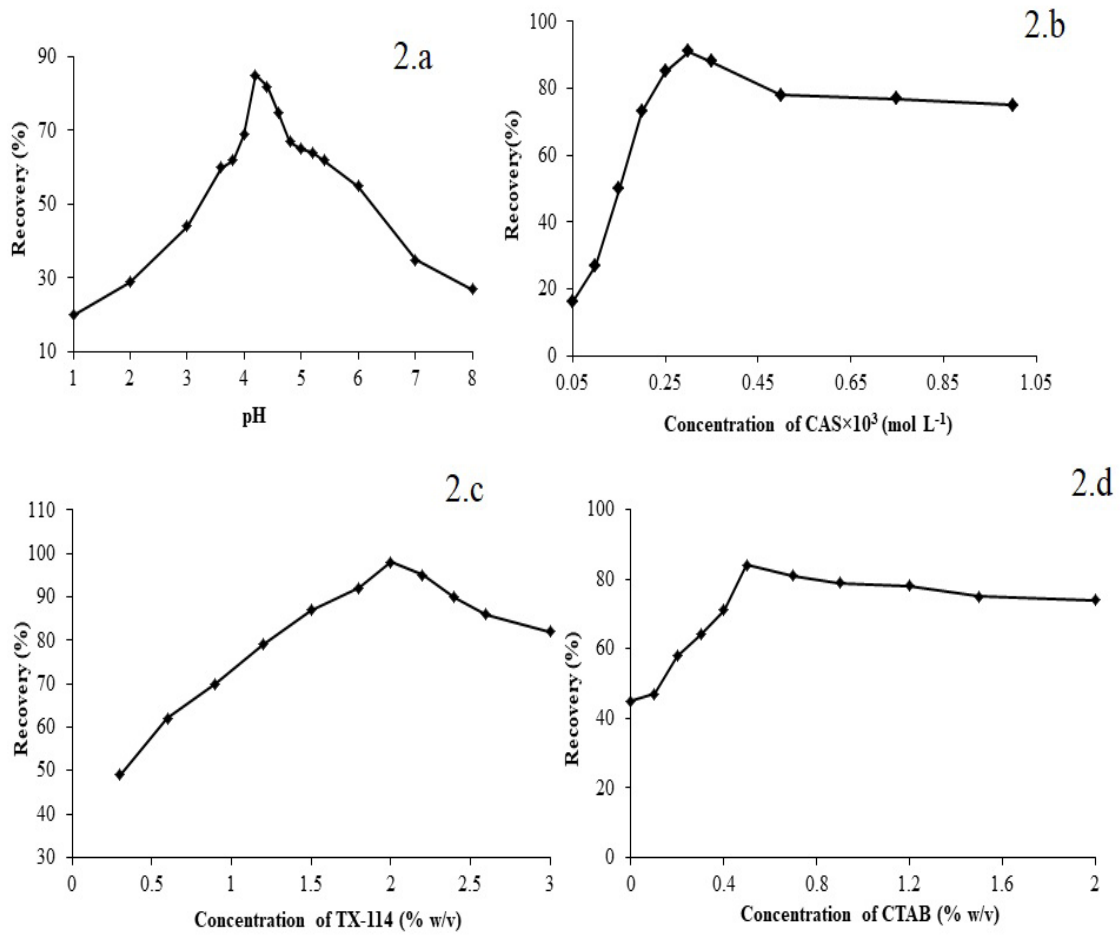

Figure 2. (a) Optimization of concentration of pH on recovery of Zr(IV), (b) Optimization of concentration of PR recovery of Zr(IV), (c) Optimization of concentration of TX-114 on recovery of Zr(IV), (d) Optimization of concentration of CTAB on recovery of Zr(IV). (Experimental conditions: pH= 4.2; [Zr(IV)] = 64.45 μg mL^{-1}; [CAS] = $0.3 \cdot 10^{-3}$ mol L^{-1}; [TX-114] = 2.0 % w/v; [CTAB] = 0.5 % w/v; [Na_2SO_4] = 2.4 % w/v; Equilibration temp. = 323 K; Equilibration time = 20 minutes).

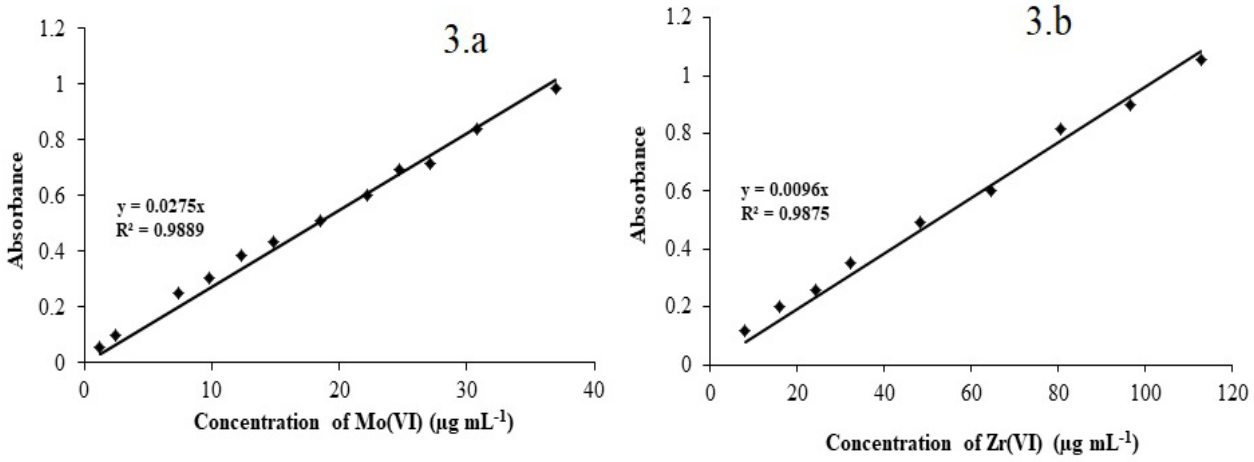

Figure 3. (a) Calibration graph for Mo(VI) under optimized conditions, (b) Calibration graph for Zr(VI) under optimized conditions.

The method's preconcentration factor stands at 13.3, while the phase volume ratio is 12.5. Comprehensive analytical performance details for the present method, encompassing both Mo(VI) and Zr(IV), are summarized in Table 1. A comparison with values reported in the literature (Table 2 and Table 3) for Mo(VI) and Zr(IV) determination indicates superior limits of detection in the current method.

Applications

The proposed mixed micellar cloud point extraction method was successfully applied for the simultaneous determination of Mo(VI) and Zr(IV) in river water and coastal water samples (Table 4) and spike recoveries in the range 87% -101% were obtained.

Table 1. Analytical figures of merit for the method (n=3).

Parameter	Mo(VI)	Zr(IV)
λ_{max} (nm)	608	546
Linear range (μg mL^{-1})	1.23 – 37.0	8.05 –112.78
Correlation coefficient (R^2)	0.988	0.987
LOD (ng mL^{-1})	1.24	9.92
Preconcentration factor	13.3	12.5
Phase volume ratio	0.081	0.086
Extraction efficiency (%)	91	94

Table 2. Comparison of the proposed method with other methods for the determination of Mo(VI).

Reagent	LOD	Pretreatment	Matrix	References
4-Nitrocatechol + tetrazolium blue	0.2 μg mL^{-1}	Liquid-liquid extraction	Steels and ferromolybdenum	[16]
Pyrogallol red	1.43 μg L^{-1}	Ionic liquid-based dispersive liquid-liquid micro extraction	water and plant leaves samples	[17]
Thiocyanate/MTOAC	5 μg L^{-1}	Surfactant-mediated liquid-liquid extraction	environmental and biological samples	[18]
Oxalate/Nile blue A	0.86 μg L^{-1}	Cloud point extraction method (CPE)	milk, vegetables and foodstuffs	[19]
Pyrogallol Red	1.24 ng mL^{-1}	Cloud point extraction method (CPE)	Tap water and sea water samples	Present work

Table 3. Comparison of the proposed method with other methods for determination of Zr(IV).

Reagent	LOD	Pretreatment	Matrix	References
4-chloro-*N*-(2,6-dimethyl-phenyl)-2-hydroxy-5-sulfam-oylbenzamide (Xipamide)	45.1 μg L^{-1}	Spectro-photometry	water and biological plant leaves and soil samples	[20]
5-Br-PADAP/ fluoride	44 μg L^{-1}	Dispersive liquid-liquid micro extraction	Water and soil	[21]
Arsenazo-III	0.48 μg L^{-1}	Solid Phase extraction	Water, soil, plant material and ore	[22] Triton X-114 = 0.20%, equilibrium time 10 min and cloud point 45 °C
2-(2-benzothiazolylazo)-3-hy-droxyphenol	150 ng L^{-1}	Solid Phase extraction	Water and soil	[23]
Chrome Azurol S	9.92 ng mL^{-1}	Cloud point ex-traction method (CPE)	Tap water and sea water samples	Present method

Table 4. Determination of Mo(VI) and Zr(IV) in the real samples and their spike recoveries in the present proposed method.

Samples	Spiked (μg mL^{-1})		Detected (μg mL^{-1})		Recovery (%)	
	Mo(VI)	Zr(IV)	Mo(VI)	Zr(IV)	Mo(VI)	Zr(IV)
	-	-	*ND	*ND	-	-
Tap water	12.3	32.45	12.20±0.09	32.85±0.07	99±0.73	101±0.23
	24.7	64.45	24.78±0.08	59.36±1.06	100±0.35	92±1.64
	-	-	*ND	*ND	-	-
Sea water	12.3	32.45	11.28±0.17	31.72±0.49	92±1.41	98±1.52
	24.7	64.45	25.03±0.69	56.27±1.23	101±2.80	87±1.91

*ND : Not Detected

Conclusions

A new method for cloud point extraction, employing a blend of surfactants (TX-114 and CTAB), has been developed to improve the preconcentration of Mo(VI) and Zr(IV) ions. Subsequent spectrophotometric analysis was utilized for quantification across various water samples. This approach is direct, highly sensitive, and accurate, harnessing the benefits of cloud point extraction (CPE). Cloud point methodologies are recognized for their simplicity, safety, speed, and cost-effectiveness. Efficient separation and pre-concentration of the target species are achieved, yielding favorable enrichment factors and low limits of detection (LOD). The method enabled the detection of Mo(VI) and Zr(IV) ions at concentrations as low as ng mL^{-1}.

Unlike certain traditional pre-concentration techniques, this method does not rely on organic solvents, thereby reducing environmental impact. Instead, it utilizes a small quantity of surfactants, readily available at low cost. Overall, this method provides a dependable and eco-friendly means of detecting trace levels of Mo(VI) and Zr(IV) species in water samples, effectively addressing both analytical and environmental concerns.

Acknowledgements

SAK thanks University Grants Commission (UGC), India, for financial support under SRF scheme (Ref. No. 30-09-2015-118875).

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