Analytical Methods

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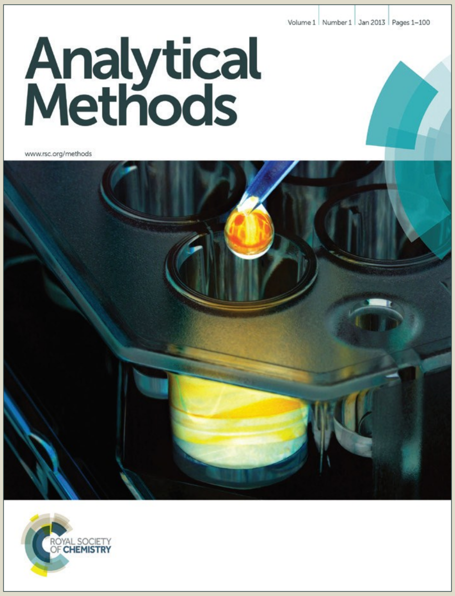

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Determinations of cobalt in the high-salinity reverse osmosis concentrate using flame atomic absorption spectrometry after cold-induced aggregation microextraction

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The main objective of this paper is to evaluate the applicability of cold-induced aggregation microextration (CIAME), followed by flame atomic absorption spectrometry (FAAS) for determination of cobalt in the high-salinity reverse osmosis concentrates. In this method, $NaPF_6$ was added to the sample solutions (50 °C) containing very small amount of 1-hexyl-3-methylimidazolium tetrafluoroborate ([Hmim][BF_4]). After cooling, a cloudy solution containing the fine droplets of the hydrophobic and robust extraction phase ([Hmim][PF_6]) were formed. Through centrifugation, the fine droplets of extractant phase were settled to the bottom of the conical-bottom glass centrifuge tube. High density and low solubility of the extraction phase in the presence of an ion pairing agent (PF_6^-) led to successful phase separation even in the high salinity solution (NaCl, 40 % w/v). α-Nitroso β-naphtol was chosen as a complexing agent. Experimental parameters were investigated and optimized. Under the optimum conditions and using 10 ml of sample, limit of detection (LOD) of 0.8 μg L^{-1}, inter-day relative standard deviation (R.S.D) of 1.78 % at the concentration of 20 μg L^{-1} and the enhancement factor of 95 were obtained. Validation of the method was performed by analysis of a certified reference material and comparison of results with those obtained by ASTM standard method (D 3558). In addition, the concentrate sample was spiked to assess matrix effect. The relative recovery at the spiking level of 20 μg L^{-1} was 94.7 %, showing no matrix interferences.

1. Introduction

Due to depletion of surface water resources, groundwater is increasingly becoming an important source of drinking water. Groundwater in many areas can have a high ionic strength due to seawater infiltration, irrigation or overdraft that results in increased salt concentration in the aquifers [1]. In addition, the groundwater is required to be treated prior to potable use due to the presence of natural and anthropological contaminants such as heavy metals, naturally occurring radioactive materials and pesticides. Desalting technologies such as reverse osmosis (RO) membrane processes are principal methods for treating the brackish groundwater, as they are effective on the removal of almost all dissolved constituents. The reverse osmosis concentrate is a brackish waste and potentially harmful to the environment due to high content of toxic metals [2–5] which can be considered as a hazardous waste.

Nearly all desalination plants used conventional methods of concentrate disposal, including disposal to surface water, sewer, evaporation pond and disposal by deep well injection. Direct disposal of membrane concentrates to surface water is regulated by the Clean Water Act and requires a permit under the National Pollution Discharge Elimination System. But there is no regulation for the limits of heavy metals for disposal to surface waters. An increase in environmental awareness and more stringent regulations may restrict disposal options in the future. Cobalt, as one of the common toxic metals and affecting the environment, is present in the wastewater of nuclear power plants and many other industries such as electroplating, paints, pigments, electronic [6] and in the reverse osmosis concentrates. The low amounts of cobalt may lead to toxic effects such as vasodilatation, flushing and cardiomyopathy in humans and animals [7–9].It also has adverse effect on the aquatic life. To protect freshwater aquatic life from acute and toxic effects of cobalt, it is recommended that

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the interim maximum concentration of total cobalt should not exceed 110 and 4 µg/L, respectively[10].

Determination of metals has been performed by different techniques, including atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS) and UV-Vis spectrophotometry. However, determination of metals in the water samples is usually requires a preconcentration step before detection due to low concentrations of the elements and high salinity matrix of samples [11,12].

The research for novel sample preparation procedures has led to development of new methods such as cloud point extraction (CPE) [13–16], dispersive liquid–liquid microextraction (DLLME) [17–19], solidified floating organic drop microextraction(SFODME) [20–23], single drop microextraction[24] and hollow fiber based-liquid phase microextraction (HF-LPME)[25]. The main advantages of the mentioned techniques are their high speed and negligible volume of solvent used.

Increase of salt content in sample solution leads to a decrease in diffusion rate of analyte from bulk solution to the extractant phase, increase in solubility of extractant phase and increase in sample density which have adverse effects on the extraction recovery, phase separation and settlement of fine droplets of extractant phase[26].

The properties of ionic liquids (ILs), such as non-volatility, adequate viscosity and thermal stability, make them an attractive alternative to other organic solvents. Liquid-phase microextraction techniques based on ionic liquids (ILs) have been recently applied for preconcentration and determination of metals[27–30].Among the preconcentration techniques, cold-induced aggregation microextraction (CIAME), which was proposed by Baghdadi and Shemirani, proved to be a robust procedure against high content of salt [31]. In this technique, an ionic liquid is dissolved in the sample at elevated temperature. A cloudy solution is formed by cooling the sample.

In CIAME, there is no interface between water and extractant phase. During the formation of fine droplets of the extractant phase, the extractant phase collect the hydrophobic species, and the extraction process is complete after formation of the droplets. As a result, mass transfer from saline solution into separated phase has no adverse effect on the extraction recovery[32]. On the other hand, In the presence of high content of salt, the solubility of ILs increases and phase separation cannot occur. However, according to the common ion effect, the solubility of ILs decreases in the presence of common ion which make phase separation possible. The fine droplets of extractant phase can be settled easily in saline solutions due to high density of ILs [26] CIAME was applied to the extraction of toxic metals in water samples [33–37]

The main objective of this paper is to study the applicability of CIAME followed by flame atomic absorption spectroscopy (FAAS) for determination of cobalt in the high-salinity reverse osmosis concentrates. The effective parameters such as pH, the amount of water-soluble ionic liquid, ion pairing agent, complexing agent and salt content were investigated and optimized. This methodology was certified according to the standard test method for cobalt in water (ASTM, D 3558, Test method B: Chelation-extraction and atomic absorption), also the sample of concentrate was spiked to assess the matrix effect.

2. Experimental

2.1. Instrumentation

An atomic absorption spectrophotometer (Varian AA-400) equipped with an air–acetylene burner and cobalt hallow-cathode lamp was used for determination of cobalt in ionic liquid phase. The operating parameters were set as recommended by the manufacturer. Measurements were carried out in the peak height mode at 240.7 nm using a spectral bandwidth of 0.2 nm. Background correction was carried out using a deuterium lamp. A Universal 320R centrifuge equipped with a swing out rotor (12-place, 5000 rpm, Cat. No. 1628A) was obtained from Hettich (Kirchlengern, Germany). A Metrohm digital pH-meter (model 692, Herisau, Switzerland) equipped with a glass-combination electrode and a water bath (WNB-14 Memmertn, Germany) were used for experiments.

2.2. Reagents

All reagents used were of analytical grade. α-Nitroso β-naphtol , acetone, 1-hexyl-3-methylimidazolium tetrafluoroborate ([Hmim][BF_4])and all salts used were obtained from Merck (Darmstadt, Germany). Sodium hexafluorophosphate ($NaPF_6$) purchased from ACROS (Geel, Belgium). All aqueous solutions were prepared in double-distilled deionized water (Millipore, USA). A solution of 0.01 mol L^{-1} of chelating agent, α-Nitroso β-naphtol, was prepared by dissolving the appropriate amount in acetone. The viscosity of ILs is high and their handling is difficult, so working solution of [Hmim][BF_4] (0.6 mg μL^{-1}) was prepared in acetone. A solution of 120 mg mL^{-1} $NaPF_6$ was prepared by dissolving appropriate amount of $NaPF_6$ in doubly distilled water. Working standard solutions of cobalt was obtained by appropriate stepwise dilution of the stock standard solution (1000 mg L^{-1} as nitrate salt).

2.3. Reverse osmosis (RO)concentrate

The reverse osmosis concentrate was collected from a RO process in Iran. As can be seen in Table 1, the pH value of the concentrate was 7.5 with a TDS concentration of 17400 mg L^{-1}. Aliquots (10 mL) of sample solution were subjected to the CIAME methodology as described above.

Table 1 Composition of the high-salinity reverse osmosis concentrate

Parameters	unit	Value
Conductivity	µs cm^{-1}	27000
pH	-	7.5
Turbidity	NTU	2.3
TDS	mg L^{-1}	17400
Na^+	mg L^{-1}	4350
Ca^{2+}	mg L^{-1}	870
Mg^{2+}	mg L^{-1}	588
Cl^-	mg L^{-1}	8900
SO_4^{2-}	mg L^{-1}	820

2.4. CIAME procedure

10 mL of the sample or standard solution containing Co^{2+}, α-Nitroso β-naphtol (1.5×10^{-4} mol L^{-1}) and [Hmim][BF_4] (30 mg) was transferred to 10 mL screw-cap conical-bottom glass centrifuge tube. After adjusting pH to 1 and warming the solution to 50 °C, one mL of $NaPF_6$ (120 mg mL^{-1}) was added to the sample solution. The obtained solution was cooled in an ice bath and a cloudy solution was formed. Then, the mixture was centrifuged for 6 min at 5000 rpm. As a result, the fine droplets of IL settled at the bottom of the centrifuge tube. Bulk aqueous phase was removed by a pipette. By re-centrifuging, the remaining sample solution on the surface of tubes was separated and removed completely. Afterwards, IL-phase was dissolved in 100 µL of methanol and then was aspirated into the flame atomic absorption spectrometer and peak height was measured as the absorbance signal.

3. Result and discussion

3.1. Selection of diluting agent

Diluting agent has to be able to dissolve ionic liquid phase, completely. On the other hand, the diluting agent should have good nebulization and burning characteristics and compatibility with direct injection into FAAS. Methanol was preferred to acetone and acetonitrile due to compatibility with the flame atomization system. By increasing the volume of diluting agent, the absorbance decreases due to decrease of cobalt concentration. On the other hand, at the low volume of diluent, the viscosity of solution is too high to aspirate efficiently in flame[38]. Therefore, in order to enhance sensitivity and enrichment factor of method, the effect of volume of the diluting agent was investigated in the range of 50-250 µL. As can be seen in Fig. 1, the absorbance increased by decreasing the volume of the diluting agent. The maximum absorbance was observed at 50 µL of diluent. Because of poor Repeatability at low volume of diluent, 100 µL of methanol was chosen to dilute the extraction phase. Due to low volume and high volatility of diluent (methanol), the samples should be diluted just before injection to the flame. Otherwise, the accuracy and precision of the method will decrease.

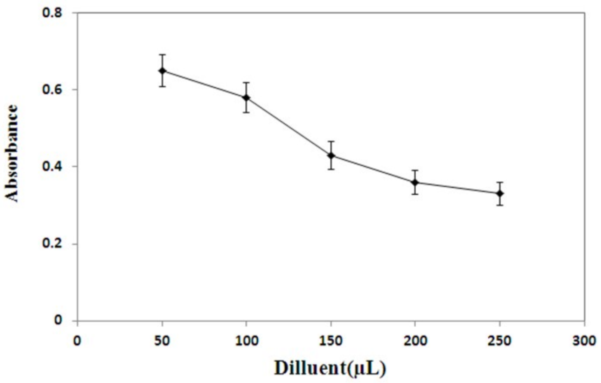

Fig. 1 Effect of diluent volume on the absorbance
Conditions: Cobalt 25 µg L^{-1}, pH=1, [Hmim][BF_4] 60 µL of 0.6 mg µL^{-1}, $NaPF_6$ 0.8 mL of 120 mg mL^{-1} Diluting agent 100 µL.

3.2. Effect of pH and α-Nitroso β-naphtol

Separation of metal ions involves prior complex formation with sufficient hydrophobicity to be extracted into the small volume of the IL-phase. pH plays a unique role on the metal-chelate formation and subsequent extraction. The effect of pH on the complex formation and extraction of cobalt from water samples was studied in the range of 1.0-6.0 using H_2SO_4 and NaOH. The results reveal that the absorbance is nearly constant in the studied range of pH. The complex of α-Nitroso β-naphtol with Co (II) is formed in weakly acidic solution (pH ≥ 4), which is oxidized rapidly due to the large stabilization associated with a low-spin d^6 electronic configuration. The oxidized form of the complex is highly resistant to dissociation in the strong acidic media. On the other hand the most metal complexes are dissociated in the acidic media and their interferences are eliminated. Therefore after complex formation in weakly acidic media, the solution was acidified to pH=1. The effect of α-Nitroso β-naphtol on the absorbance is shown in Fig. 2.

The result showed that the absorbance of cobalt increased by increasing the concentration of complexing agent up to 1.5×10^{-4} mol L^{-1} which is due to shift in equilibrium toward the complex formation. A concentration of 1.5×10^{-4} mol L^{-1} was chosen as the optimum. In order to overcome the possible interference effects of other metals, a higher concentration of complexing agent is proposed.

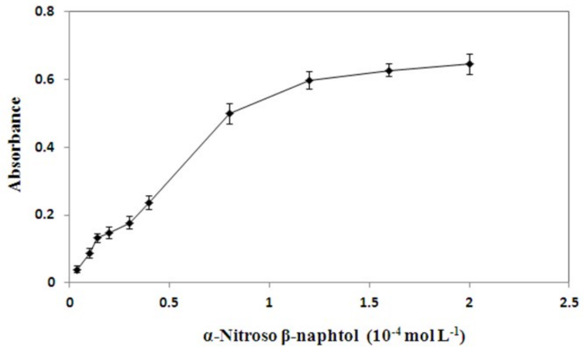

Fig. 2 Effect of α-Nitroso β-naphtol on the absorbance.
Conditions: Cobalt 25 µg L^{-1}, pH=1, [Hmim][BF_4] 60 µL of 0.6 mg $µL^{-1}$, $NaPF_6$ 0.8 mL of 120 mg mL^{-1}, Diluting agent 100 µL.

3.3. Effect of $NaPF_6$ and [Hmim][BF_4]

The effect of $NaPF_6$ was investigated in the range of 0.2-1.2 mL (120 mg mL^{-1}) in the presence of 30 mg of [Hmim][BF_4] and the results are shown in Fig. 3a. According to the common ion effect, by increasing the amount of NaPF6 up to 0.5 mL, the solubility of [Hmim][PF_6] decreases and extractant phase is formed, so extraction recovery and absorbance increases. At the low amount of $NaPF_6$ the extractant phase is not sufficient for complete extraction of analyte. Over 0.5 mL $NaPF_6$, the absorbance is nearly constant, because the volume of extractant phase remains constant. One mL of $NaPF_6$ was chosen for the subsequent experiments in order to have a robust extraction system against high content of salt.

The effect of [Hmim][BF_4] was studied in the range of 10-80 µL (0.6 mg $µL^{-1}$) in the presence of 120 mg of NaPF6. The minimum [Hmim][BF_4] amount required for the formation of cloudy solution was 10 µL.

By increasing the amount of [Hmim][BF_4], the absorbance decreases (Fig. 3b) which is due to increase in the volume of the settled phase and dilution of extractant phase. On the other hand, by increasing the volume of settled IL-phase, viscosity of the IL-methanol mixture increases which can lead to decrease in the aspiration rate of solution into the flame and decrease in absorbance signal []. Therefore, 50 µL of [Hmim][BF_4] was chosen for the subsequent experiments.

3.4 Effect of salt content

In the presence of high content of salt, the solubility of ILs increases and phase separation does not occur. However, according to the common ion effect ($\mathbf{[Hmim][PF_6]} \leftrightarrow \mathbf{Hmim^+} + \mathbf{PF_6^-}$) , the solubility of ionic liquid decreases in the presence of common ion (PF_6^-). NaCl and $NaNO_3$ were chosen in order to study the salt effect. Due to higher solubility of $NaNO_3$, salt effect can be studied up to 50 % (w/v). As it is shown in Fig. 4, in the presence of the excess of $NaPF_6$, phase separation occurred successfully up to 40 % (w/v). Due to high density of ILs, the fine droplets of IL phase can be settled- even in the high salinity solutions

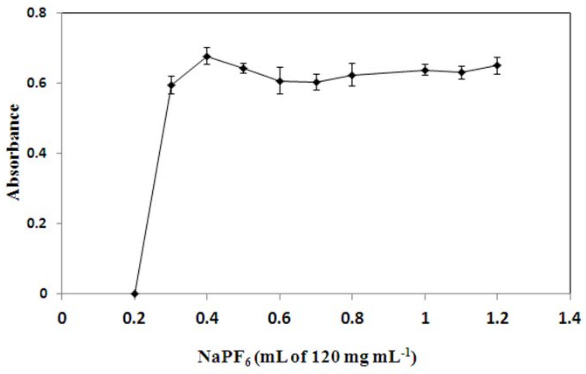

Fig. 3a Effect of $NaPF_6$ on the absorbance.
Conditions: Cobalt 25 µg L^{-1}, α-Nitroso β-naphtol 75 µL of 0.01 mol L^{-1}, pH=1, [Hmim][BF_4] 60 µL of 0.6 mg $µL^{-1}$, Diluting agent 100 µL.

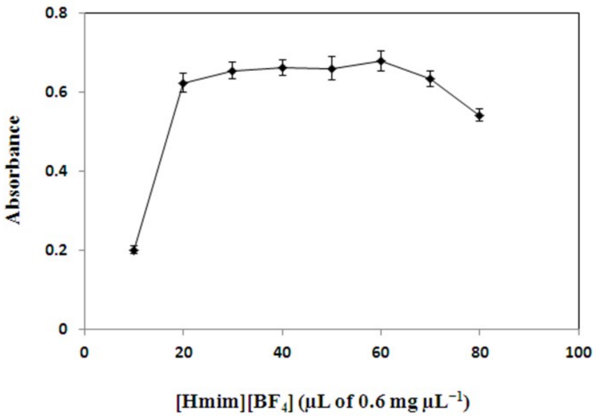

Fig. 3b Effect of [Hmim][BF_4] on the absorbance.
Conditions: Cobalt 25 µg L^{-1}, α-Nitroso β-naphtol 75 µL of 0.01 mol L^{-1}, pH=1, $NaPF_6$ 1mL of 120 mg mL^{-1}, Diluting agent 100 µL.

3.5 The effect of centrifuge conditions

The effect of centrifugation rate on the absorbance was studied in the range of 1000 - 5000 rpm. It was found that the over 4000 rpm, IL-phase completely settled, so the rate of 5000 rpm was selected as the optimum point. At the optimum rate, the absorbance was investigated as a function of centrifugation time. Over 5 min, absorbance was constant, indicating complete transfer of IL-phase to the bottom of centrifuge tube. So, the optimum centrifugation time was chosen as 6 min.

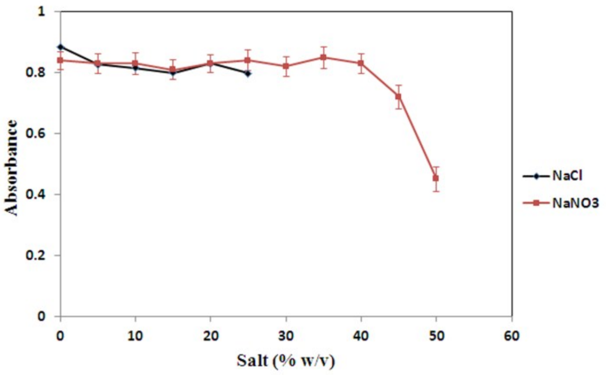

Fig. 4 Effect of NaCl and $NaNO_3$ on the absorbance.
Conditions: Cobalt 25 µg/L, α -Nitroso β-naphtol 75 µL of 0.01 mol L^{-1}, pH=1, [Hmim][BF_4]] 50 µL of 0.6 mg µg L^{-1}, $NaPF_6$ 1mL of 120 mg mL^{-1} ,Diluting agent 100 µL.

3.6 Selectivity of the method

The interference effect of a wide variety of anions and cations was investigated by spiking the appropriate amounts of the relative ions to a reference Co (II) solution of 25 µg L^{-1}. A species resulting in ± 5 % variation in absorbance was considered as interfering agent. No adverse effects were observed at 100000 times higher than Co(II) from Na^+ , Cl^- , Ca^{2+}, Mg^{2+} ,SO_4^{2-}, and at 1000 times higher than Co(II) from the various cations and anions examined (I^- Br^-, Li^+, K^+, Ba^{2+}, Sr^{2+} Ag^+, Cd^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+}, Pb^{2+} , Al^{3+}, Cr^{3+}, Fe^{3+}) at the presence of 5×10^{-4} mol L^{-1} of α-Nitroso β-naphtol.

3.7 Figures of merit

Table 2 summarizes the analytical characteristics of the optimized method, including limit of detection, reproducibility and enhancement factor. The limit of detection (LOD= 0.8 µg L^{-1}) was calculated as 3Sb/m (Sb: standard deviation of the blank signals; m: slope of calibration curve after preconcentration). A good correlation coefficient (r=0.993) was obtained and acceptable deviations between sequential determinations (R.S.D=1.78 %) were found at 25 µg L^{-1} of Co (II). The calibration curve was investigated up to 50 µg L^{-1}, which was linear. Enhancement factor (EF=95) was obtained from the slope ratio of calibration curve after and before preconcentration.

Table 2 Analytical characteristics of the method

	Co with	Co without
Slope	2.40×10^{-2}	2.53×10^{-4}
Intercept	0.008	0.029
Correlation	0.993	0.996
R.S.D (%) (n=5)[a]	2.6(10),1.78 (20)	1.80 (500)
LOD (µg L^{-1})[b]	0.8	30
Enhancement	95	-

[a] Values in parentheses are the Co(II) concentration (µg L^{-1}) for which the RSD was obtained.
[b]Determined as 3 S_B/m (where S_B and m are the standard deviation of the blank signal and the slope of the calibration graph, respectively).
[c]Calculated as the slope ratio of the calibration graph obtained with and without preconcentration.

3.8. Validation of the method and determination of cobalt in RO concentrate

The proposed methodology was applied for the determination of cobalt in RO concentrate. In order to validate the accuracy and precision of the method, RO concentrate and related spiked samples were analyzed by CIAME. This methodology was certified according to the ASTM test method for cobalt in water (D 3558-Test method B: Chelation-extraction and atomic absorption). Certified and obtained values and high recoveries of cobalt show no matrix interferences (Table 3). Significance testing was performed for comparing two mean values obtained by two methods. The critical value for t (0.05, 10) is 2.23. Since t_{exp}(0.34) is less than critical value for t, it can be concluded that two methods are not significantly different at the significance level of 0.05.

For further verification the accuracy of the method, a certified reference material (SCP-ES-L-1, Groundwater) was analyzed according to the proposed method. It was found that the analytical results were in good agreement with the certified values (Tables 4), no significant differences have been observed.

Table 3 Determination of Co (II) in RO concentrate and relative recoveries of spiked samples

Method	Found (µg L^{-1}) mean±S.D *	Added (µg L^{-1})	Found (µg L^{-1}) mean±S.D *	Recovery (%)
CIAME	33.1± 2.1	15.0	47.3± 7.1	94.7
ASTM	28.5± 1.0	15.0	44.8± 8.2	108.7

*Standard deviation (n=6).

Table 4 Determination of cobalt in a standard reference material

Certified reference material	SCP-ES-L-1
Certified* (µg L^{-1})	51±1
Foundd (µg L^{-1})	49±2
Recovery (%)	96.1

* Mean value±S.D. based on five replicate measurements.

Table 5 Comparison of CIAME with other methods for determination of cobalt in water samples

Determination technique	Preconcentration method	Sample volume (mL)	Diluent volume (µL)	Enhancement factor	LOD (µg L^{-1})	Reference
Spectrophotometry	SPE	100	5000	100	3.1	[39]
HPLC	SPE	200	1000	200	0.05	[40]
FAAS	DLLME	6	50	120	3.8	[41]
FAAS	CPE	50	2000	25	1	[42]
FAAS	SPE	250	3000	83.3	0.37	[43]
FAAS	SPE	50	5000	8.3	1.2	[44]
Spectrophotometry	CPE	40	3000	23	0.6	[45]
FAAS	Micro-SPE	50	1000	50	0.8	[46]
FAAS	CPE	50	2000	25	2.4	[47]
FAAS	CIAME	10	100	95	0.8	Present

3.9. Comparison of CIAME with other methods

Determination of cobalt in RO concentrate by CIAME and FAAS was compared with other methods and the results are shown in Table 5. As can be seen, the LOD of the proposed method with the lower sample volume is better than that of others.

4. Conclusion

CIAME is a simple and robust sample preparation technique against very high content of salt (up to 40 %) which can be applied for brines, seawater and Ro concentrates. The applicability of proposed method was evaluated through determination of cobalt in high-salinity reverse osmosis concentrate. The results showed the proposed method was successfully applied for determination of cobalt in RO concentrate with TDS of 17400 mg L^{-1}. Under the optimum conditions and using 10 ml of sample, the limit of detection (LOD) of 0.8 µg L^{-1}, relative standard deviation (R.S.D) of 1.78 % and the enhancement factors of 95 were obtained. This methodology was certified according to the standard test method for cobalt in water (ASTM, D 3558).

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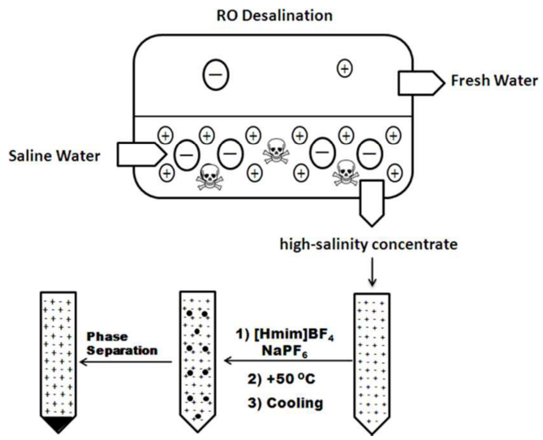

Cold-induced aggregation microextraction (CIAME) is a robust procedure for high-salinity reverse osmosis concentrates.