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Determination of Chromium in Different Water Samples Using Cloud Point Extraction (CPE) Coupled with Flame atomic Absorption Spectrometry (FAAS)

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ABSTRACT

Cloud point extraction was applied as a Preconcentration of chromium after formation of complex with 4-((1-hydroxynapthalen-2-yl) methyleneamino)-2-hydroxybenzoicacid (HNMAHBA), and later determined by Flame atomic absorption spectrometry (FAAS). Using octyl Phenoxy polyethoxy ethanol (TritonX-114) as surfactant. Chromium was complexed with HNMAHBA in an aqueous phase and was kept for 10 min in a thermostated bath at 50^0C. Separation of the two phases was accomplished by centrifugation for 15 min at 2500 rpm. The chemical variables affecting the cloud point extraction were evaluated, optimized and successfully applied to chromium determination in various water samples. Under the optimized conditions, the preconcentration system of 100mL samples permitted an enhancement factor of 50-fold. The detailed study of various interferences made the method more selective. The detection limits obtained under optimal condition was 0.59µgmL^{-1}. the extraction efficiency was investigated at different Chromium concentrations (4.0-20.0µgmL^{-1}) and good recoveries (98.6-106.0%) were obtained using present method.. the proposed method has been applied successfully for the determination of Chromium in various water samples and compared with reported and spectrophotometric methods in terms of Student's 't'-test and variance ratio 'f'-test which indicate the significance of present method over reported and spectrophotometric methods at 98% confidence level.

Keywords: Chromium; 4-((1-hydroxynapthalen-2-yl) methyleneamino)-2-hydroxybenzoicacid (HNMAHBA); Cloud point extraction (CPE); Tritonx-114; Flame atomic absorption spectrometry (FAAS) and water samples.

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INTRODUCTION

Recently interest in the medical and industrial significance of platinum, and to a lesser extent palladium and chromium, has been accompanied by an increasing interest in their determination at low levels. Consequently, much effort was invested in the development of analytical methods Possessing sufficient detection capacity. Several analytical techniques (ETAAS, NAA, ICP-AES, & ICP-MS) are available for determination of trace metal ions in natural water. These techniques were was highly expensive and sophisticated. This draw back can rectified by combination of a suitable preconcentration technique with subsequent determined by flame atomic absorption spectrometry (FAAS) determination. Cloud point extraction is a facile, rapid and versatile technique employed for pre-concentration and analysis of pesticides, polychlorides and phenols [1, 2]. The technique is based on the property of most non-ionic surfactant in aqueous solutions to form micelles and become turbid when heated to a temperature known as cloud point temperature (CPT). Above the cloud point, the micellar solution separates into a surfactant-rich phase of a small volume and in a diluted aqueous phase, in which the surfactant concentration is close to the critical micellar concentration (CMC). The small volume of the surfactant-rich phase obtained with this methodology permits the design of extraction schemes are facile, economical, highly efficient and of lower toxicity than extraction with the use organic solvents. 8-hydroxyquinoline was used as a complexing agent in cloud point extraction coupled with AAS [3, 4], ICP-AES [5], FAAS [6], and ICP-MS [7], in natural water samples.

In the present study, a reagent 4-((1-hydroxynapthalen-2-yl) methyleneamino)-2-hydroxybenzoicacid (HNMAHBA) was synthesized for the cloud point extraction and Preconcentration of chromium from water samples. The method was based on the complexation of chromium with4-((1-hydroxynapthalen-2-yl) methyleneamino)-2-hydroxybenzoicacid (HNMAHBA) in presence of TritonX-114 at pH 8.0±0.2 using either HCl or NaOH. Optimum experimental conditions were investigated with respect to a standard solution of the same matrix, in order to examine the possibility to obtaining the maximum extraction efficiency with minor sample treatment and minimal experimental conditions. This is an alternative method to the solid phase extraction and column techniques for the analysis of metal ions in various samples of environmental importance.

MATERIALS AND METHODS

Reagents and Solutions

Doubly distilled water and high purity reagents were used for all preparations of the standard and sample solutions. All chemicals were purchased from Merck chemicals. Mumbai, India. Standard stock solution of chromium nitrate and potassium dichromate (dissolved in 0.5 M HNO_3) was prepared by dissolving the proper amounts of analyte in double distilled water in a 100mL flask. Dilute solutions were prepared by the appropriate dilution of the stock solution daily in doubly distilled water for reference solutions. The non-ionic surfactant, TritonX-114

(Merck chemicals, Mumbai, India.) was used without further purification. 0.005M of 4-((1-hydroxynapthalen-2-yl) methyleneamino)-2-hydroxybenzoicacid (HNMAHBA) was dissolving 0.67864gm in100mL of doubly distilled water. Equimolar solution of solution of NaOH and HCL were added appropriately to get desirable pH of 8.0 ± 0.2. Buffer solution pH 6.0 (for spectroscopic method) was prepared by adding concentrated sulfuric acid (3.4mL) to 250 mL distilled water in a 500mL flask. Then monosodium dihydrogen phosphate monohydrate (25g) was added and the flask shaken until dissolution was completed. The solution was then diluted to 500mL.

Synthesis of 4-((1-hydroxynapthalen-2-yl) methyleneaminohydroxybenzoicacid (HNMAHBA)

0.01M of 1-hydroxynapthalene-2-carbaldehyde dissolved in methanol. Added to 0.01M of 4-amino-2-hydroxybenzoicacid in methanol. Then the solution is refluxed 2 hours .Then cooled to room temperature. Pale yellow precipitated collected and washed with cold ethanol the product was purified by recrystalisation from ethanol.

General procedure

For cloud-point extraction, aliquots of the cold solution containing the analyte, 0.12 % of TritonX-114 and 6.0×10^{-5} M HNMAHBA was adjusted to pH 8.0±0.2 with phosphate buffer. At this pH, the recovery of one species Cr (III) is highest and that of the other one Cr (VI) is lowest. The total system was placed for 10 min in a thermostat bath at 50^0C. The separation of the two phases was achieved by centrifugation at 2500 rpm. The phases were cooled in an ice bath in order to increase the viscosity, the surfactant-rich phase. The aqueous phase was decanted by inverting the tube. To decrease the viscosity, the surfactant rich phase was dissolved in 700 mL of methanolic solution containing 0.1 M HNO_3. The resultant final solution was directly introduced in to the spectrometer through conventional aspiration. The total chromium was determined as Cr (III) by the method described above after reducing Cr (VI) to Cr (III). The reduction of Cr (VI) to Cr (III) was carried out by adding 0.3 mL 6 N concentration H_2SO_4 and 0.3 mL of ethanol (95%(w/v)) to the sample solution. Then the concentration of Cr (IV) was calculated by subtracting the concentration of Cr (III) from the total chromium concentration.

Determination of chromium species in water Samples

The data obtained from the present method for the preconcentration and cloud point extraction applied for spiked and natural water samples are represented in Table 1 The results were compared with the reported method are summarized in Table 1 in terms of student t-test and variance ratio of f-test. It is found that percentage recovery of chromium (III) and (VI) from water samples ranges from 98.6 to 106.0%, which is more reliable and sensitive than the reported method. The validity of the present method was checked by analyzing the certified reference material and the results are shown in Table 4. The analytical data obtained from the present method is in good agreement with certified values and it shows the accuracy of the

present method. It is evident from the data in Table.1 that the proposed method is rapid, more sensitive and selective.

Table-1: Determination in synthetic mixtures of Cr (III) and Cr (VI)[a]

Added (μgmL^{-1})		Found (μgmL^{-1})		Recovery [b] (%)	
Cr (III)	Cr (VI)	Cr (III)	Cr (VI)	Cr (III)	Cr (VI)
0.2	0.2	0.19	0.19	98.2±1.2	99.1±1.5
0.2	0.4	0.19	0.40	98.3±1.5	98.7±1.5
0.4	0.8	0.39	0.79	97.9±1.2	99.0±1.4
0.5	1.0	0.50	0.98	99.4±1.1	98.3±1.6

[a] Sample volume 100mL [b] Mean of three determinations

RESULTS AND DISCUSSIONS

Pyrolysis and Atomization Temperature Curves

Pyrolysis and Atomization Temperature Curves was investigated in the range of 400-1300^{0}C and 1800-2800^{0}C respectively. When the Pyrolysis temperature was close to 650^{0}C, the maximum relative integrated absorbance was achieved. When the temperature was further increased, relative integrated absorbance decreases, increasing the atomization temperature to 2400^{0}C, the absorbance reached to the maximum. So, the Pyrolysis temperature of 650^{0}C(fig.2a) and atomization temperature of 2400^{0}c (fig2b) were selected for further studies

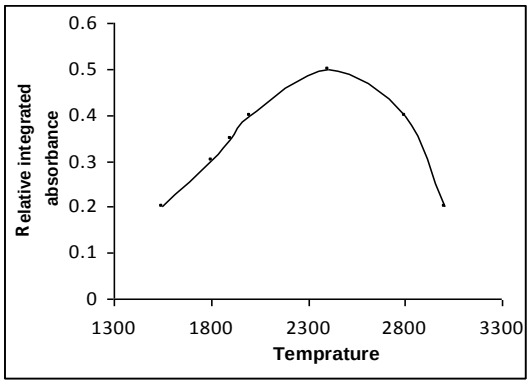

Fig.2 (a). Pyrolysis curve for the CPE .

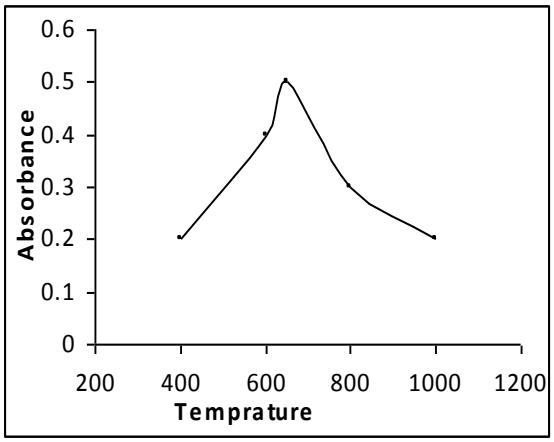

Fig.2 (b). Atomization curve for the CPE

Effect of pH

Cloud point extraction of chromium was performed with different pH values. The results presented in the Figure 3 show the effect of pH on extraction of chromium complex. It is seen that extraction was quantitative for chromium in the pH range of 7.0-9.0. Hence, a pH of 8.0±0.2 was chosen for subsequent investigations.

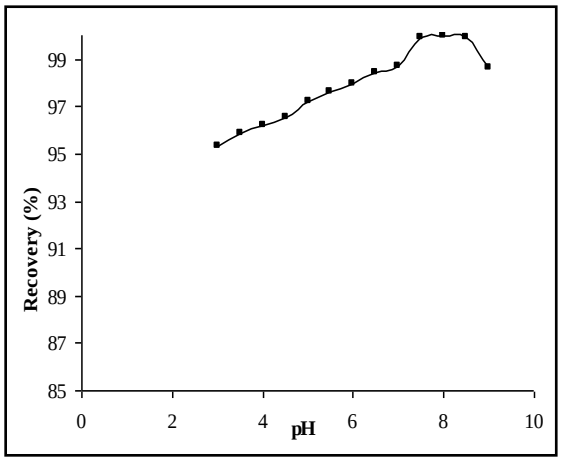

Fig.3. Effect of pH on CPE of recovery of chromium

Effect of reagent concentration

The effect HNMAHBA concentration on the determination of chromium was investigated in the range of 0.01-0.08 M. The results are shown in Figure 4. A concentration of 0.05 M was chosen as the optimum concentration for the subsequent studies.

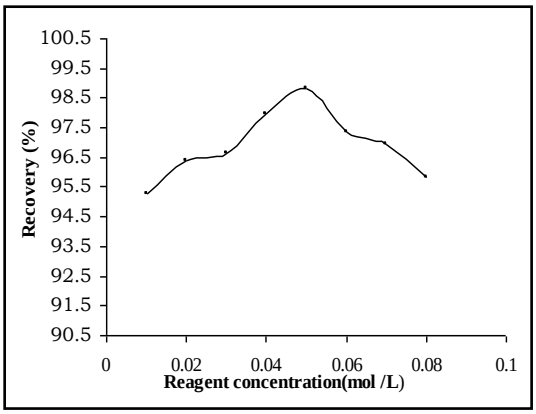

Fig.4. Effect of reagent concentration on recovery of metal ion

Effect of Triton X-114 concentration

Triton X-114 was chosen for the formation of the surfactant rich phase due to its low cloud point temperature (23-25^{0}C) and high density of the surfactant rich phase, which facilitates easy phase separation by centrifugation. It was found that the Triton X-114 gave effective extraction of the chromium in liquid samples in the concentration range of 0.12% (w/v). With an increase of Triton X-114 concentration above and below 0.12% (w/v), the signal strength decreased. The results are shown in Figure 5 the optimum surfactant concentration for the chromium determination was chosen as 0.2% (w/v) Triton X-114, in order to achieve the optimal signal strength.

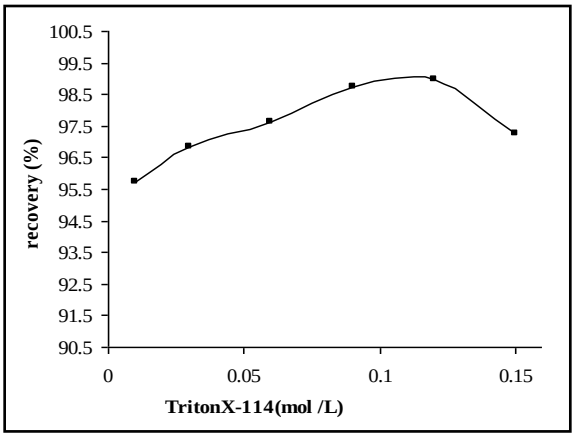

Fig.5. Effect of Triton X-114 concentrations on recovery of metal ion

Effect of equilibrium temperature and incubation time

Optimal equilibration temperature and incubation time were necessary to complete the reaction and to achieve easy phase separation and preconcentration of chromium. The effect of equilibration temperature on the extraction recovery of chromium was investigated in the range of 30-60^{0}C. It was found that the extraction recovery increased with equilibration temperature from 30^{0}C and stabilized at 60^{0}C. 40^{0}C was ensuring maximum signals. Therefore

the temperature of 40^0C was employed and the influence of the incubation time on cloud point extraction was monitored in the range of 5-20min. It was found that 10 minutes of incubation time was optimal for the separation process.

Effect of viscosity on analytical signal

In order to decreases the viscosity of the surfactant rich phase to facilitate easy handling and introduction into the nebulizer of the FAAS, the methanol solution containing 0.1M nitric acid was added to the surfactant rich phase, It was found that there was an optimized volume of methanol (200-300 µL) with respect to the absorbance signal. For smaller added volumes of acidified methanol, the signal was lower because of the inappropriate properties of the solution for aspiration and nebulization, where as for greater volumes, there is a decrease in the signal due to dilution. Therefore 200 µL of volume of acidified methanol was used throughout the experiment in order to ensure optimal signal strength.

Calibration, precision and detection

The calibration graphs was obtained by preconcentration of 500mL of sample in the presence of 0.12% Triton X-114 under the optimum instrumental conditions as shown in Table 2 These analytical parameters derived for the present method are shown in Table 3 The standard deviation ranged from 0.019 to 0.17, the limit of detection was satisfactory and found to be 0.59µg mL^{-1}.In this case the preconcentration of 500 mL of sample in the presence.

Table-2: Experimental conditions

Lamp current (mA)	15
Wave length (nm)	358
Slit (nm)	1.4
Cuvette coated material	Zr
Gas flow/mL min^{-1}	35
Sample volume (mL)	500

Table-3: Analytical characteristics

Parameters	Analytical features for Cr
Preconcentration factor[a]	89
Correlation coefficient	0.9997
Regression equation C (μL^{-1})	$Y=21.4x\ 10^3 +0.005$
Limit of Detection (µg mL^{-1})	0.59
Linear range (μL^{-1})	0.25-3.75
S.D (n=10) [b]	0.17

[a] ratio of the concentration of anylate without the application of CPE technique: n=10

Effect of foreign ions

The influence of foreign ions on the determination of chromium was studied and an error of ± 2 % in absorbance reading was considered tolerable. Sample solution containing chromium (50 g L^{-1}) and other ions were prepared and the developed procedure was applied. The tolerance limits of various foreign ions are given in Table 5.and the results prove that the recoveries of analyte ions were almost quantitative in the presence of interfering cat ions.

Table-5: Effect of foreign ions

Ions	Concentration(mgL^{-1})
Na^{+}, K^{+}	20000
Ca^{2+}	200
Mg^{2+}	100
Ag^{+}, Al^{3+}	10
Mn^{2+}	6
Cu^{2+}, Fe^{3+}	5
Cd^{2+}, Pb^{2+}	3
Ba^{2+}, Hg^{2+}, Ni^{2+}, Zn^{2+}	2
Co^{2+}	1

Application of present method and statistical Comparison with Report Method

The data obtained with the proposed method for the preconcentration and cloud point extraction employed for the spiked and natural water samples were present in Table. 4. Unusually high concentrations of chromium in river water and Tap water samples. The obtained result was compared with reported method. The analytical data summarized in Table 4 Suggest that the percentage of chromium recovery from water samples ranges 99.0%. This is more reliable and sensitive than the other methods.

Table-4: Recovery of Chromium from water samples using CPE technique

Sample	Added		Present method Found(μgL^{-1})		Recovery(%)[a]		'f' &'t' -test
	Cr(III)	Cr(IV)	Cr(III)	Cr(IV)	Cr(III)	Cr(IV)	
Tap water[a]	-	-	0.20	--	--	--	--
	4.0	4.0	4.20	--	101.0±0.32	103.5±0.27	0.20 &1.50
	10.0	10.0	10.20	--	102.3±0.30	99.5±0.39	0.66 &2.05
Spiked water	10	10	20.2	-	105.10±0.33	99.9±0.37	0.57 &4.34
	15	15	14.90	14.80	99.3±0.37	98.6±0.27	----

[a] Collected tap water from Chickballapur town area, Karnataka

Present method was compared with the reported methods in the literature in terms of detection limits and instruments employed for the analysis of metal ions in various environmental samples. It is evident from the above data that the proposed method is facile, rapid and more sensitive.

Table-6 Comparison of the present method with reported methods for CPE of Chromium

Reagent	Surfactant	Technique	Detection limit	References
1-(2-thiozolylazo)-2-Napthol	TritonX-114	FAAS	0.24(ngMl^{-1})	[8]
Ammonium Pyrroline dithiocarbamate	TritonX-114	G FAAS	0.1-2.0(µgmL^{-1}	[9]
1-(2-pyridylazo)-2-napthol	TritonX-114	FAAS	0.38(ngmL^{-1})	[10]
2-(5-bromo-2-pyridylazo 5(diethylamino)-phenol	TritonX-114	GFAAS	0.08(µgmL^{-1}	[11]
8-hydroxyquinoline	TritonX-114	G FAAS	0.012(ngmL^{-1})	[12]
1-nitriso-2-napthol	PONPE 7.5	FAAS	1.22(µgmL^{-1})	[13]
N-benzoyl-N-phenyl hydroxylamine	TritonX-114	FAAS	2.08(ngmL^{-1})	[14]
1-phenyl-3-methyl-4-benzoyl-5-pyrazolone	TritonX-114	FAAS	0.64(ngmL^{-1})	[15]
4-((1-hydroxynapthalen-2-yl) ethylene amino) -2-hydroxybenzoicacid	TritonX-114	FAAS	0.59(ngmL^{-1})	Present work

CONCLUSION

The cloud point extraction offers a simple, rapid, sensitive, inexpensive, non-polluting and environmentally benign methodology which is alternative to other separation /pre-concentration techniques. Triton X-114 was chosen for the formation of the surfactant rich phase due to its excellent physico-chemical characteristics. The present method has been successfully applied for the determination of chromium in water samples. This method has the following added advantages over already reported methods. (Table-6).

1. The synthesis of metal chelating agent in the laboratory is simple and more economical.
2. The synthesis of organic reagent is distancing in terms of sensitivity, selectivity towards metal ions.
3. The risk of contamination is quite low.
4. Foreign ions do not method gives very low LOD, good SD's and solvent free extraction of the elements from its initial matrix.

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