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Hexavalent chromium recovery by liquid–liquid extraction with 2-octylaminopyridine from acidic chloride media and its sequential separation from other heavy toxic metal ions

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Abstract   A systematic study of extraction of chromium(VI) with 2-octylaminopyridine (2-OAP) in xylene at room temperature has been conducted. Quantitative extraction of chromium(VI) was observed in the 0.4–0.8 M concentration range of hydrochloric acid. From the extracted complex species in the organic phase, chromium(VI) was back extracted with 7 N ammonia (3 × 10 mL), and was determined by spectrophotometric method. Various parameters such as 2-OAP concentration, equilibrium period, effect of various diluents, aqueous: organic volume ratio, acidity and diverse ions were studied. The extraction reaction proceeds with ion-pair formation and the stoichiometry of extracted species was found to be $[(2OAPH^+) \ CrO_3Cl^-]_{(org)}$. The separation and determination of chromium(VI) from associated and toxic metals in binary, ternary and multicomponent mixture were carried out. The method permits the sequential separation of chromium(VI) from other toxic metals and has been used to separate and determine chromium(VI) from alloys, and effluent water samples from tannery industries.

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1. Introduction

Chromium is used for the production of stainless steel, chrome plated metals, pigments and chemicals. The main chromium emissions into surface water are from metal-finishing processes such as electroplating pickling and bright dipping. Uncontrolled emissions are potential contaminating sources in fresh waters, especially with regard to the toxic chromium(VI). Other discharges of chromium(VI) are related to the additives

in circulating cooling waters, laundry chemicals and animal glue manufacture (Pannain and Santelli, 1995). Owing to the high oxidation potential and the ease of penetration from biological membranes, chromium(VI) compounds are approximately 100 times more toxic than chromium(III) salts. Moreover, in environment air, chromium particulates play a role in the oxidation of sulphur dioxide and the formation of acidic aerosols involved in global acid rain (Bag et al., 2000).

Toxicity of chromium compounds depends on its oxidation state (Goldoni et al., 2006). Chromium(VI) compounds were found to be toxic for living organisms. Human toxicity includes lung cancer as well as kidney, liver and gastric damage, hence chromium(VI) is one of the major toxic element present in environmental samples (Kozlowski et al., 2002). In view of these facts, the separation and determination of chromium at trace levels have received considerable attention for the ease of manipulation and routine operation.

High molecular weight amines (HMWA's), termed as 'liquid anion exchangers', are used in liquid–liquid extraction for many metals as they have low water solubility and high miscibility in organic solvents. The quaternary ammonium salts such as trioctylmethylammonium compounds (aliquat 336) (Lo and Shiue, 1998), alamine 336 and aliquat 336 (Vincent and Guibal, 2000) and alamine 336 (Senol, 2004) played important role in liquid–liquid extraction of chromium(VI). Chromium(VI) has been extracted with liquid anion exchanger, amberlite LA 1 and LA 2 in methyl isobutyl ketone (MIBK) from waste water and sludge (Stasinakis et al., 2003), urine (Claudio et al., 1983) and aerosol particles (Nusko and Heumann, 1997). Liquid–liquid extraction of chromium(VI) from sulphuric acid solution with tri-*n*-dodecylamine (Jamal, 2007) containing octanol-1 as a modifier in kerosene was investigated. Separation and recovery of chromium(VI) from simulated plating waste aqueous solution using microcapsules consisting of styrenedivinylbenzene copolymer and containing tri-*n*-octylmethylammonium chloride (TOMAC) or bis (2-ethylhexyl) phosphoric acid (D2EHPA) as the extractant were studied (Nishihama et al., 2004).

The chromium(VI) was complexed by the reaction with ammonium pyrolidine dithiocarbamate (APDC). The chromium(VI) complex in organic extract was determined by HPLC (Wang and Chiu, 2004) and inductively coupled plasma mass spectrometry (Li et al., 2002). The determination of hexavalent chromium in fresh and saline waters is based on the reaction of chromium(VI) with diphenyl carbazide (DPC) (Gardner and Comber, 2002). An on-line dynamic two dimensional admicelles solvent extraction system was coupled to electrothermal atomic absorption spectrometry (ETAAS) for determination of chromium(VI) with pyrolidine dithiocarbamate (Nan and Yan, 2005) in drinking water. The content of chromium(VI) in water was determined by air-acetylene FAAS after being enriched by ammoniumpyrolidinedithiocarbamate-diethyldithiocarbamate-methyl *iso*butyl ketone APDC (Xiuxiang et al., 1999)/DDTC (Xiuxiang et al., 1999; Tang et al., 2004)/ MIBK (Tang et al., 2004) system in which APDC and Na-DDTC were complexing agents and MIBK was extracting agent. Diperoxochromium creates a complex with ethyl acetate (Beni et al., 2007) while, chromium(III) remains in the aqueous phase. The chromium(VI) content of ethyl acetate phase was determined with graphite furnace atomic absorption spectrometry. The reported method was applied for the separation of chromium(VI) from chromium(III).

A supported liquid membrane (SLM) technique was investigated for extraction and pre-concentration of chromium(VI) by using aliquat 366 (Lorraine et al., 2002).

The economic recovery and concentration of chromium(VI) from waste water was investigated using an emulsion liquid membrane (ELM) containing aliquat 336 chloride (Datta and Agrwal, 1999; Bhowal and Datta, 2001; Chakraborty et al., 2005a,b; Banerjea et al., 2000) as an extractant and SPAN 80 as surfactant. An attempt has been made to extract chromium(VI) through emulsion liquid surfactant membrane or emulsion liquid membrane (ELM) from its acidic solution, using alamine336 (Chakraborty et al., 2005a,b) and caustic soda as an extractant and stripping reagent, respectively. Around 97% extraction of chromium(VI) from aqueous solutions of potassium dichromate through batch experimentation has been achieved.

Extraction of chromium(VI) from sulphuric acid aqueous solution using a liquid surfactant membrane (LSM) containing tributyl phosphate (TBP) (Chiha et al., 2006; Vohra et al., 1989) was studied. The influence of the sodium hydroxide concentration on stripping efficiency was investigated. The extraction of chromium(VI) through a liquid surfactant membrane, tributyl phosphate (TBP) and trioctylphosphinoxide (TOPO) (Frites et al., 2005) dissolved in dodecane considered as a carrier was reported. Triethanolamine was used as an inner phase reagent. The solvent extraction of chromium(VI) in chloroform, dichloromethane, dichloroethane and its transport through a chloroformic bulk liquid membrane from sulphuric acid solutions with neutral extractant triphenyl phosphine (TPP) (Sachmoune and Mitiche, 2004) was studied. The co-extraction and the co-transport of sulphuric acid is very low and has no effect on the transport efficiency. The extraction of hexavalent chromium from aqueous solution by cocob betaine (Singh et al., 2002) in a mixture of kerosene and benzene was investigated. In acidic solution the extraction efficiency of chromium(VI) was excellent. However, the relative affinities of NO_3^-, Cl^- and SO_4^{2-} to cocob betaine were also considerable. Synthesis of calix [4] arene diamide derivatives (Bozkurt et al., 2005) was reported and used for the extraction of chromium(VI). The complexation ability of calix [4] arene was studied and it was based on the receptors.

In view of all the above, separation and determination of chromium(VI) have been receiving considerable attention by researchers. 2-OAP synthesized by Borshch, Petrukhin method (Borshch and Petrukhin, 1978) has been reported as an effective extractant for lead(II) (Mane and Anuse, 2008) from this laboratory. In continuation of this work, in the present paper, a systematic study of extraction of chromium(VI) with 2-OAP in xylene at room temperature has been reported.

2. Experimental

2.1. Apparatus

An Elico-digital spectrophotometer model SL-171 (Elico India Limited, Hyderabad) with 1 cm quartz cells was used for absorbance measurement. An Elico digital pH meter model LI-120 (Elico India Limited, Hyderabad) was used for pH measurements. Tapson's analytical single pan balance model 200 T having accuracy 0.001 g was used for weighing operations.

2.2. Reagents

2.2.1. Chromium(VI) solution (CrO_4^{2-})

A 1 mg/mL chromium(VI) solution was produced by dissolving 3.735 g of dry potassium chromate (BDH) in distilled water and diluted to 1000 mL. It was standardized by suitable method (Vogel, 1961).

2.2.2. 2-Octylaminopyridine solution (0.036 M)

A 0.036 M 2-OAP solution was produced by dissolving 0.750 g of crystalline 2-OAP in xylene and diluted to 100 mL.

2.2.3. Diphenyl carbazide solution (0.25%)

It is prepared by dissolving 0.250 g of the reagent (Loba) in 1:1 acetone containing 1 mL of 1:10 sulphuric acid and diluted to 100 mL, the solution was kept in an amber coloured glass bottle.

The working solutions were prepared by accurate dilutions and standardization. A double distilled water was used for the preparation of solutions and their dilutions throughout all the experimental procedure. Analytical grade chemicals i.e. Loba, Merck, BDH and s-d fine were used.

2.3. General extraction procedure for the extraction of chromium(VI)

To an aliquot containing 25 μg chromium(VI) in 25 mL volumetric flask enough hydrochloric acid was added to get the concentration of the solution 0.5 M. The solution was diluted to 25 mL up to the mark and transferred into a 125 mL separatory funnel. The aqueous phase was equilibrated with 10 mL of 0.036 M 2-OAP solution in xylene for 5 min. The two phases were allowed to separate. The aqueous phase was washed with 5 mL xylene and was rejected. The organic phase was back-stripped with three 10 mL portions of 7 N ammonia. The solution was evaporated till it remains 1/4th. The chromium(VI) from the solution was determined by spectrophotometric method using diphenyl carbazide (Cotton and Wilkinson, 1972; Greenwood and Earnshaw, 1984) at 540 nm. The amount of chromium(VI) was computed from the calibration curve.

3. Results and discussion

3.1. Effect of acidity

The extraction of 25 μg of chromium(VI) from different concentrations of acid media with 0.036 M 2-OAP in xylene was carried out by keeping the aqueous to organic volume ratio 2.5:1. The extraction of chromium(VI) was 14.3% at 0.01 M hydrochloric acid and becomes quantitative in the range of 0.4–0.8 M hydrochloric acid and again there was decrease in the extraction of chromium(VI) with increasing the acidity. It may be due to the formation of stable hydrochloride with 2-OAP. The percentage extraction (% E) and distribution ratio (D) are calculated by using following expressions:

$$\%E = (\text{Metal extracted/Metal taken}) \times 100 \qquad (i)$$

$$D = [\%E/(100 - \%E)]$$
$$\times [(\text{Volume of aqueous phase/Volume of organic phase})] \qquad (ii)$$

The extraction was found to be incomplete from perchloric, hydrobromic, nitric, sulphuric and acetic acid media, Table 1. However, for proposed method 0.5 M hydrochloric acid concentration was recommended.

3.2. Extraction of chromium(VI) as a function of 2-OAP concentration

The extraction of 25 μg of chromium(VI) from 0.5 M hydrochloric acid solution by 2-OAP in xylene within the range 0.0048–0.4850 M 2-OAP was studied at 25 °C. The extraction of chromium(VI) was found to increase with increasing reagent concentration. The extraction was quantitative in the concentration range of 0.024–0.073 M of 2-OAP. Further increase in concentration of 2-OAP decreased the extraction of chromium(VI). The decrease in the extraction is due to the formation of stable ion-pair complex between 2-OAP and chloride. However, in this procedure in order to ensure complete extraction of chromium(VI), 0.036 M 2-OAP concentration was recommended.

3.3. Extraction of chromium(VI) as a function of diluents

The extraction of chromium(VI) was performed from 0.5 M hydrochloric acid medium using 10 mL of 0.036 M 2-OAP in various aliphatic and aromatic diluents, like benzene, toluene, xylene, chloroform, carbon tetrachloride, 1,2-dichloroethane, methyl isobutyl ketone (MIBK), n-butanol, amyl acetate, amyl alcohol and kerosene, Table 2. The extraction of chromium(VI) was found to be quantitative in xylene, while in other diluents there was incomplete extraction of chromium(VI). No correlation between dielectric constant and percentage extraction was observed.

3.4. The influence of equilibrium time

The shaking time was varied from 0.25 to 20 min. It was observed that the extraction of chromium(VI) was 78.8% at 0.25 min, which was further increased and became quantitative in the range of 4–7 min. With prolonged shaking time the percentage extraction decreased due to dissociation of the ion-pair complex due to agitation. For proposed method 5 min equilibration time was recommended in order to ensure the complete extraction of metal ion.

3.5. Loading capacity of 2-OAP

The loading capacity of the extractant was determined by the repeated contact of organic phase with a fresh feed solution of the metal of same concentration. For a 10 mL, 0.036 M solution of 2-OAP in xylene at 0.5 M hydrochloric acid concentration and a A/O of 2.5:1, the maximum loading capacity for chromium(VI) was found to be 75 μg at 25 °C.

3.6. Effect of aqueous to organic volume ratio

The results of contacting different volumes ratios of aqueous to organic phase have been investigated. The study indicated that a preferred aqueous to organic (A/O) phase ratio in the study was 7.5:1 or less. This is evident from the sharp increase in the extraction efficiency as well as distribution ratio of chromium(VI) when phase ratio was changed from 25:1 to

Table 1 Extraction of chromium(VI) as a function of acid concentration Cr(VI) = 25 μg; 2-OAP = 0.036 M in xylene; Aqueous: organic volume ratio = 25:10; Equilibration time = 5 min; Strippant = 7 N NH$_3$ (3 × 10 mL).

Acid, M	HCl		HClO$_4$		HBr		HNO$_3$		[b]H$_2$SO$_4$		CH$_3$COOH	
	% E	D	% E	D	% E	D	% E	D	% E	D	% E	D
0.01	14.3	0.42	3.2	0.082	14.4	0.42	3.5	0.09	13.7	0.40	22.2	0.71
0.05	63.3	4.31	6.1	0.16	36.8	1.45	3.1	0.08	17.7	0.54	27.9	0.97
0.1	84.1	13.22	2.9	0.07	52.9	2.81	4.5	0.12	21.8	0.70	27.2	0.93
0.2	86.8	16.43	3.0	0.08	58.2	3.48	4.7	0.12	25.8	0.87	29.1	1.03
0.3	90.6	24.10	3.0	0.08	68.9	5.54	5.6	0.15	28.6	1.00	33.2	1.24
0.4	100.0	∞	5.2	0.13	62.8	4.22	8.8	0.15	24.6	0.82	34.1	1.30
0.5	100.0[a]	∞	6.3	0.17	60.3	3.80	5.9	0.16	37.0	1.47	31.1	1.13
0.6	100.0	∞	8.1	.22	56.9	3.30	5.9	0.16	36.1	1.41	29.5	1.04
0.7	100.0	∞	7.2	0.19	53.4	2.6	5.9	0.16	36.8	1.46	36.9	1.46
0.8	100.0	∞	3.9	0.10	52.9	2.81	7.2	0.19	30.9	1.12	37.4	1.49
0.9	94.8	45.57	3.8	0.10	53.1	2.83	9.1	0.25	28.1	0.98	34.1	1.29
1.0	94.0	39.16	3.4	0.09	52.9	2.81	10.1	0.28	25.6	0.86	38.1	1.53

[a] Acid concentration recommended for extraction procedure.
[b] Concentrations in normal solution.

Table 2 Extraction of chromium(VI) as a function of diluents Cr(VI) = 25 μg; 2-OAP = 0.036 M; Hydrochloric acid = 0.5 M; Aqueous: organic volume ratio = 25:10; Equilibration time = 5 min; Strippant = 7 N NH$_3$ (3 × 10 mL).

Diluent	Dielectric constant, ε	Percentage extraction, % E	Distribution ratio, D
Benzene	2.28	92.4	30.35
Xylene[a]	2.30	100.0	∞
Toluene	2.38	90.4	23.41
Methyl isobutyl ketone	13.11	86.6	16.21
n-Butanol	17.80	47.5	2.26
Amyl acetate	4.80	51.0	2.60
Amyl alcohol	13.90	25.4	0.85
Kerosene	1.80	16.3	0.49
Chloroform	4.81	85.8	15.13
Carbon tetrachloride	2.24	88.0	18.37
1,2-Dichloroethane	1.254	94.3	41.28

[a] Diluent recommended for extraction procedure.

7.5:1. This may be simply due to the unavailability of the reagent for metal extraction. So a crowding effect occurs at low phase ratio. However, in the recommended procedure the phase ratio was mentioned as 2.5:1 so as to avoid the large consumption of the hydrochloric acid.
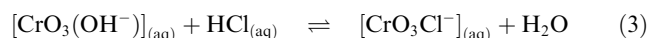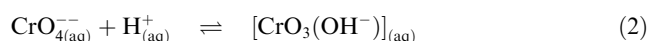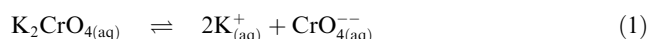
3.7. Effect of stripping agents

Various stripping agents of different concentrations were examined for the back extraction of the chromium(VI) from the organic phase, Table 3. Chromium(VI) was stripped quantitatively by ammonia solution (3 × 10 mL) in the concentration range of 7–9 N while other basic strippants like sodium hydroxide, potassium hydroxide and sodium carbonate and weak acid like acetic acid were found to be ineffective in the stripping of chromium(VI). In the proposed method 7 N (3 × 10 mL) ammonia was used as a strippant for further study.

3.8. Nature of the extracted species

Attempts were made to ascertain the stoichiometry of extracted complex species using slope analysis method, using $\log D_{[Cr(VI)]}$ against $\log C_{[2\text{-}OAP]}$ plots. A graph of $\log D_{[Cr(VI)]}$ against $\log C_{[2\text{-}OAP]}$ at 0.1 and 0.3 M hydrochloric acid concentrations gave slopes of 1.0 and 0.9 respectively, Fig. 1. The probable mechanism of the extraction appears to be protonation of 2-OAP which forms cationic species like [2-OAPH$^+$], while the chloride ions combine with chromium(VI) to form anionic species like [CrO$_3$Cl$^-$] (Marckzenko, 1976; Sandell, 1965). The probable nature of the extracted species is [(2-OAPH$^+$·CrO$_3$Cl$^-$]$_{(org)}$.

The extraction mechanism was explained as:

$$K_2CrO_{4(aq)} \rightleftharpoons 2K^+_{(aq)} + CrO^{--}_{4(aq)} \tag{1}$$

$$CrO^{--}_{4(aq)} + H^+_{(aq)} \rightleftharpoons [CrO_3(OH^-)]_{(aq)} \tag{2}$$

$$[CrO_3(OH^-)]_{(aq)} + HCl_{(aq)} \rightleftharpoons [CrO_3Cl^-]_{(aq)} + H_2O \tag{3}$$

$$2\text{-}OAP_{(org)} + H^+_{(aq)} \rightleftharpoons [2\text{-}OAPH^+]_{(org)} \tag{4}$$

$$[2\text{-}OAPH^+]_{(org)} + [CrO_3Cl^-]_{(aq)} \rightleftharpoons [2\text{-}OAPH^+CrO_3Cl^-]_{(org)} \tag{5}$$

Table 3 Extraction of chromium(VI) as a function of stripping agents Cr(VI) = 25 μg; 2-OAP = 0.036 M in xylene; Hydrochloric acid = 0.5 M HCl; Aqueous: organic volume ratio = 25:10; Equilibrium time = 5 min.

Molarity, M	NH$_3$ recovery, %	NaOH recovery, %	KOH recovery, %	Na$_2$CO$_3$ recovery, %	CH$_3$COOH recovery, %
0.5	81.5	52.7	68.7	61.8	64.6
1	88.7	59.2	80.6	81.1	66.8
2	88.2	80.8	92.3	81.8	73.1
3	89.0	81.0	62.3	82.8	62.1
4	90.1	83.1	68.7	73.9	66.9
5	93.7	88.9	60.1	67.3	66.6
6	95.0	81.4	45.3	61.4	59.8
7	100.0[a]	81.4	42.6	49.4	59.8
9	100.0	81.4	32.2	18.8	59.6
11	83.2	–	30.3	18.8	59.6

[a] Strippant recommended for general extraction procedure.
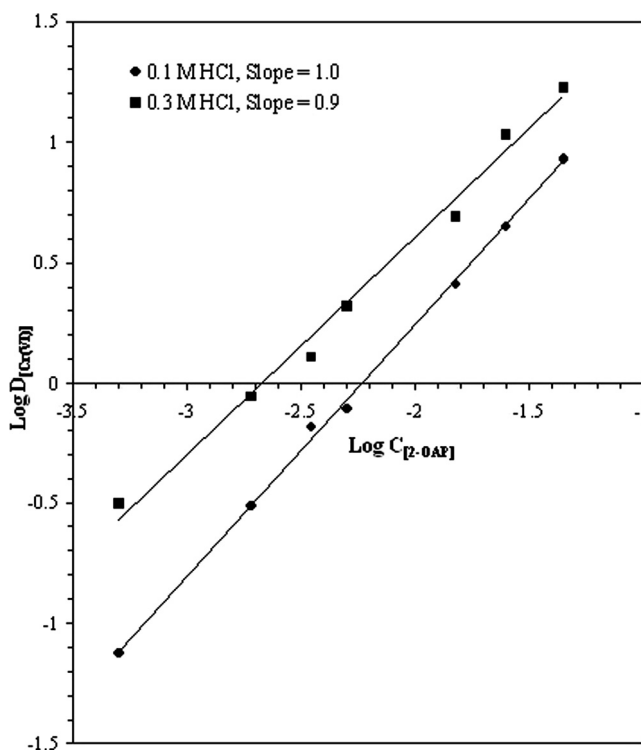
Figure 1 Log–log plot of $\log D_{[Cr(VI)]}$ versus $\log C_{[2\text{-}OAP]}$ at 0.1 and 0.3 M HCl.

3.9. Effect of various diverse ions on the extraction of chromium(VI)

In order to judge the selectivity and utility of the proposed method, chromium(VI) was extracted in the presence of several other ions. The tolerance limit was set at the amount of the foreign ion that could be present to give an error less than ±2% in the recovery of chromium(VI). It has been found that I$^-$, NO$_2^-$, SCN$^-$, S$_2$O$_3^{2-}$, thiourea, ascorbate, Te(IV), Fe(III), Cu(II), Tl(I) ions were interfered in the extraction of chromium(VI). The interference of Cd(II) and Bi(III) was eliminated by masking them with 25 mg EDTA while interference of Tl(III) and Sb(III) was eliminated by masking with 5 mg fluoride, Table 4.

4. Applications

4.1. Separation and determination of chromium(VI) from binary mixtures

The suitability of the above developed method was examined by applying it to the separation and determination of chromium(VI) in a variety of binary mixtures containing associated and toxic metal ions, e.g. Cr(III), Ni(II), Co(II), Pb(II), Zn(II), Hg(II), Mn(II) and Mn(VII). The extraction and determination of chromium(VI) from binary mixtures were carried out by taking the advantage of difference in the extraction conditions of the metal ions, Table 5.

Chromium(VI) was separated from the binary mixture of Ni(II), Mn(II), Mn(VII) and Co(II) by its extraction with 10 mL of 0.036 M 2-OAP in xylene from 0.5 M hydrochloric acid solution. Under these conditions the added metal ions remained quantitatively in the aqueous phase, while chromium(VI) was extracted in the organic phase. The aqueous phase was washed with 5 mL xylene to remove traces of the reagent. It was evaporated to moist dryness with 10 mL concentrated hydrochloric acid. The residue was dissolved in distilled water and diluted to 25 mL. The metal ion from aqueous phase was determined by the standard methods (Cotton and Wilkinson, 1972; Greenwood and Earnshaw, 1984; Marckzenko, 1976). Chromium(VI) from organic phase was back extracted with 7 N ammonia solution (3 × 10 mL) and estimated by spectrophotometric method.

The chromium(VI) was separated from the binary mixture of Cr(III), Pb(II), Zn(II) and Hg(II) by its extraction with 10 mL of 0.036 M 2-OAP in xylene from 0.5 M hydrochloric acid solution. Under these conditions the added metal ions were co-extracted with chromium(VI) in trace amount in organic phase. Separation of these metal ions was achieved by the use of masking agents. Chromium(III), Zn(II) and Hg(II) were masked with 25 mg EDTA while Pb(II) was masked by 10 mg EDTA. Under these conditions the added metal ions remained in the aqueous phase quantitatively while the chromium(VI) was extracted in organic phase. The aqueous phase was washed with 5 mL xylene. It was evaporated to moist dryness with 2 mL perchloric acid. The procedure was repeated thrice for complete demasking. The residue was evaporated with 5 mL hydrochloric acid and then with 10 mL water twice for the removal of trace amount of acid. The residue was dis-

Table 4 Effect of various diverse ions on percentage extraction of chromium(VI) Cr(VI) = 25 µg; 2-OAP = 0.036 M in xylene; Hydrochloric acid = 0.5 M; Aqueous: organic volume ratio = 25:10; Equilibrium time = 5 min.

Tolerance limit, mg	Foreign ion added
0	Iodide, nitrite, thiocyanate, thiosulphate, thiourea, ascorbate, Te(IV), Fe(III), Cu(II), T1(I)
0.100	Cr(III), Ga(III), Zn(II), Tl(III)[a], Sb(III)[a], Bi(III)[b]
0.250	Citrate, Cd(II)[b], Zn(lI)
0.50	Salicylate, oxalate, Y(III), Be(II), Sr(II), Ni(II), Sn(II), La(III), Ce(III)
1	Acetate, Hg(II), Pb(II), Se(lV), Mg(II), AI(III), Ca(II), V(V), Mn(VII), Co(II)
2	Sn(IV), Ba(II), Mn(II), In(III)
5	Fluoride, Mo(VI), W(VI)
25	Bromide
50	Nitrate, malonate
100	Phosphate, EDTA

[a] Masked by 5 mg fluoride.
[b] Masked by 25 mg EDTA.

Table 5 Separation of chromium(VI) from binary mixtures.

Metal ion	Amount taken, (µg)	Average recovery[a], %	Chromogenic ligand for determination
Cr(VI)	25	98.9	Diphenyl carbazide
Cr(III)[c]	25	99.6	Diphenyl carbazide
Cr(VI)	25	98.7	
Ni(II)	50	99.0	DMG
Cr(VI)	25	100.0	
Co(II)	100	99.0	Thiocyanate
Cr(VI)	25	98.9	
Pb(II)[b]	100	100.0	PAR
Cr(VI)	25	98.8	
Zn(II)[b]	50	100.0	PAR
Cr(VI)	25	100.0	
Hg(II)[b]	25	99.4	PAR
Cr(VI)	25	100.0	
Mn(II)	25	99.3	PAR
Cr(VI)	25	99.8	
Mn(VII)	50	100.0	PAR

[a] Average of six determinations.
[b] Masked by 10 mg EDTA.
[c] Masked by 25 mg EDTA.

solved in water, diluted to 25 mL and the metal ions from the aqueous phase were determined by standard methods (Cotton and Wilkinson, 1972; Greenwood and Earnshaw, 1984; Flaschka and Barnard, 1972). Chromium(VI) from the organic phase was back extracted with 7 N ammonia (3 × 10 mL). The aqueous phase was evaporated to one fourth of its total volume and chromium(VI) was determined by diphenyl carbazide method.

4.2. Sequential separation and determination of chromium(VI) from ternary mixtures containing toxic metals

Sequential separation of chromium(VI) from ternary mixtures of Cr(VI), Pb(II), Zn(II) and Cr(VI), Pb(II) and Hg(II) was carried out by taking advantage of extraction ability of 2-OAP with metal ions in mineral acid medium and weak organic acid medium, Table 6.

Under the optimum extraction condition of chromium(VI), Pb(II) and Zn(II) were masked with 25 mg EDTA. The masked metal ions remained in the aqueous phase, while chromium(VI) was quantitatively extracted in the organic phase which was back extracted with 7 N ammonia (3 × 10 mL) and was determined spectrophotometrically. Lead(II) and Zn(II) remained in the aqueous phase were demasked by perchloric acid, followed by hydrochloric acid treatment. The residue was dissolved in 10 mL water and evaporated to moist dryness to remove trace amount of acid. Lead(II) was separated from Zn(II) from its extraction with 10 mL of 0.036 M 2-OAP in chloroform from 0.007 M sodium succinate solution at pH 10 (Mane and Anuse, 2008). Under these conditions Zn(II) was remained quantitatively in the aqueous phase. The aqueous phase was washed with 5 mL chloroform to remove traces of the reagent. Zinc(II) from the aqueous phase was determined by standard method (Flaschka and Barnard, 1972). Lead(II) from the organic phase was backstripped with 0.4 M hydrochloric acid (3 × 10 mL) and estimated by standard method (Flaschka and Barnard, 1972).

Under the optimum extraction condition of chromium(VI), Pb(II) and Hg(II) were masked with 25 mg EDTA, while chromium(VI) was quantitatively extracted in organic phase, it was back extracted with 7 N ammonia (3 × 10 mL) and was determined by recommended procedure. Lead(II) and Hg(II)

Table 6 Sequential separation and determination of chromium(VI) from ternary mixtures.

Metal ion, μg	% Recovery[a]	Determination method
Cr(VI), 25	99.0	Diphenyl carbazide
Pb(II)[b], 50	100.0	PAR
Zn(II)[b], 50	99.5	PAR
Cr(VI), 25	99.2	Diphenyl carbazide
Pb(II)[b], 50	100.0	PAR
Hg(II)[b], 50	99.5	PAR

[a] Average of six determinations.
[b] Masked by 25 mg EDTA.

remained in the aqueous phase were demasked by perchloric acid followed by hydrochloric acid treatment. The residue was dissolved in 10 mL distilled water and evaporated to moist dryness to remove traces of acid completely. The residue containing Pb(II) and Hg(II) was dissolved in distilled water. Under the optimum extraction condition of Pb(II) there was partially co-extraction of Hg(II), but quantitative co-extraction of Hg(I). Hence Hg(II) was reduced to Hg(I) with hydroxylamine hydrochloride. Lead(II) and Hg(I) were extracted with 10 mL of 0.036 M 2-OAP in chloroform from 0.007 M sodium succinate solution at pH 10. Lead(II) was back stripped from the organic phase with 0.4 M acetic acid (3×10 mL) and determined by standard method, (Flaschka and Barnard, 1972) while Hg(I) remained quantitatively in organic phase was converted into Hg(II) by warming the organic phase with bromine water. Mercury(II) was back extracted with 2 N HCl (3×10 mL) and determined by standard method (Flaschka and Barnard, 1972).

4.3. Validity of method

To study applicability of the proposed method for the real samples, the method was employed for the analysis of chromium(VI) present in real samples like alloys, Table 7 and waste water samples from tannery industries, Table 8.

4.3.1. Determination of chromium(VI) from alloy
The proposed method is applicable for the analysis of alloys for chromium(VI) content. An alloy sample was dissolved in 15 mL *aqua-regia* and was evaporated to moist dryness. The procedure was repeated thrice with 5 mL concentrated perchloric acid for complete oxidation of Cr(III) to Cr(VI). The residue was cooled and extracted with 10 mL water. The solution was filtered through Whatmann filter paper No.1. The filtrate was diluted to 100 mL with distilled water. Chromium(VI)

Table 7 Analysis of alloys.

Alloy	Composition, %	Cr(VI), recovery[a], %	RSD, %
Ni/Cr Chromyl positive	Ni, 10 Cr, 90	98.5	1.5
BCS-287 Non ferrous alloy	Cr, 12.46 Mo, 6	99.4	0.6
NBS-153 A Tool steel	Cr, 4 Y, 2 Mo, 9 Co, 8	99.4	0.6

[a] Average of six determinations.

was extracted and determined from the sample solution by proposed method, Table 7. There is good agreement between the amount found and certified value.

4.3.2. Analysis of chromium(VI) from waste water sample from tannery industries
The five water samples were collected from the drainages of tannery industries. One water sample was collected from Jayanti nala in the area of tannery industries in Kolhapur city.

One litre of each water sample colleted in a plastic drum was taken in a 1000 mL beaker. It was filtered through ordinary filter paper by which floating and suspended matters were removed. The samples were boiled till reduced to volume about 500 mL, by which organic and coloured matters were decomposed, cooled and allowed to stand to settle down the residue. The solution was filtered through Whatmann filter paper No.1 and was washed for three times with distilled water. The filtrate along with washings were collected in 1000 mL beaker and evaporated till moist dryness. The residue was evaporated till moist dryness with 10 mL concentrated hydrochloric acid with stirring and was repeated till effervescence of CO_2 disappears for complete decomposition of Na_2CO_3. The residue was evaporated with 10 mL of perchloric acid (for complete oxidation of Cr(III) to chromium(VI) present in residue). The residue was dissolved in water and diluted to 100 mL. A sample solution containing chromium(VI) was produced.

An aliquot of sample solution was taken in a 25 mL volumetric flask. It was mixed with hydrochloric acid to make the concentration of solution to 0.5 M in 25 mL and extracted with 10 mL 0.036 M 2-OAP in xylene for 5 min. Chromium(VI) was quantitatively extracted in organic phase and was back extracted by 7 N ammonia solution (3×10 mL) and was determined by recommended procedure. Chromium(VI) from the sample solution was also determined by AAS method. The results obtained by the proposed method were in close agreement with those of the values obtained by the AAS method, Table 8.

5. Conclusion

The important features of the method described here are:

(i) It permits selective separation of chromium(VI) from other toxic and associated metal ions such as Cr(III), Ni(II), Co(II), Pb(II), Zn(II), Hg(II), Mn(II) and Mn(VII).

(ii) Low reagent concentration (0.036 M) is required for the quantitative recovery of chromium(VI) as compared with other high molecular weight amines.

(iii) It is free from the interference of large number of foreign ions which are commonly associated with chromium(VI) in its natural occurrence.

(iv) 2-OAP extracts chromium(VI) in xylene from hydrochloric acid media by anion exchange mechanism in which a complex of stoichiometric formula $[2\text{-}OAPH^+ CrO_3Cl^-]_{(org)}$ is formed

(v) It is applicable to the analysis of chromium(VI) in synthetic mixtures, alloy samples, effluent water from tannery industries in Kolhapur city.

(vi) The developed method is very simple, selective, reproducible and rapid, requires less time for the separation and determination of chromium(VI).

Table 8 Determination of chromium(VI) from waste water from tannery industries at Jawahar Nagar and Jayanti Nala, Kolhapur city.

Sample	Cr(VI) found by proposed method, μg/L	Cr(VI) found by AAS, μg/L	Recovery[a], %	RSD, %
Sample 1	0.073	0.074	98.9	1.06
Sample 2	0.064	0.064	99.9	0.10
Sample 3	0.093	0.095	98.0	1.97
Sample 4	0.419	0.420	99.8	0.18
Sample 5	0.116	0.116	100.0	0.00
Sample 6	0.020	0.020	100.0	0.00

[a] Average of six determinations.

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