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Speciation, liquid–liquid extraction, sequential separation, preconcentration, transport and ICP-AES determination of Cr(III), Mo(VI) and W(VI) with calix-crown hydroxamic acid in high purity grade materials and environmental samples

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Abstract

A new functionalized calix[6]crown hydroxamic acid is reported for the speciation, liquid–liquid extraction, sequential separation and trace determination of Cr(III), Mo(VI) and W(VI). Chromium(III), molybdenum(VI) and tungsten(VI) are extracted at pH 4.5, 1.5 M HCl and 6.0 M HCl, respectively with calixcrown hydroxamic acid (37,38,39,40,41,42-hexahydroxy7,25,31-calix[6]crown hydroxamic acid) in chloroform in presence of large number of cations and anions. The extraction mechanism is investigated. The various extraction parameters, appropriate pH/M HCl, choice of solvent, effect of the reagent concentration, temperature and distribution constant have been studied. The speciation, preconcentration and kinetic of transport has been investigated. The maximum transport is observed 35, 45 and 30 min for chromium(III), molybdenum(VI) and tungsten(IV), respectively. For trace determination the extracts were directly inserted into the plasma for inductively coupled plasma atomic emission spectrometry, ICP-AES, measurements of chromium, molybdenum and tungsten which increase the sensitivity by 30-fold, with detection limits of 3 ng ml^{-1}. The method is applied for the determination of chromium, molybdenum and tungsten in high purity grade ores, biological and environmental samples. The chromium was recovered from the effluent of electroplating industries.

Keywords: Speciation; Preconcentration; Sequential separation; Cr; Mo; W; Calix-crown; Hydroxamic acid

1. Introduction

Chromium, molybdenum and tungsten are important constituents of modern alloys and these elements are quite abundant in untreated waste waters of iron, steel, leather tanning, metal plating, battery, electro wiring, metal finishing, aerospace and electronic industries. The heavy metal emissions are of increasing importance is assessment of risks associated with a combustion system. Metal contributes about 7–9% of a typical waste by weight, a significant fraction of incombustible matter in hazardous waste. Atmospheric emission of Cr, Mo, As, Cu, Ni etc. and their salts are regulated under the clean act. Many of these, like Cr, Mo emitted into the atmosphere pose serious health hazards. The bioinorganic chemistry of chromium, molybdenum and tungsten plays an important role in biological systems [1]. Since these are the essential elements contributing to the function of 11 known enzymes, their accurate determination in blood plasma is important to obtain an insight into their metabolism. It passes continuation risk to natural environment concern because of its toxicity [2]. In contrast, Cr(VI) is carcinogenic and can diffuse through cell membrane and oxidize molecules with toxic results [3,4].

In recent year, it has become recognized that trace metal analysis must involve the metal speciation in addition to total metal analysis. Biomedical, biological and toxicological

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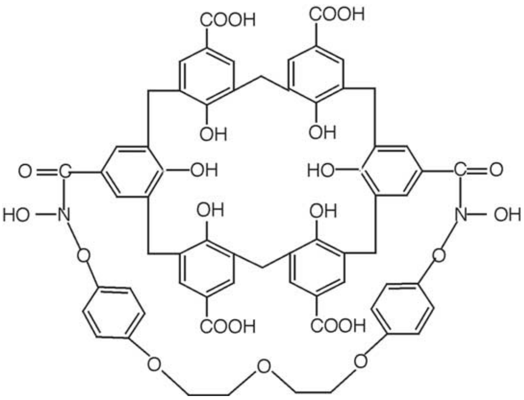

Fig. 1. 37,38,39,40,41,42-hexahydroxy-7.

properties depend upon the specific form in which, the metal is present and combinations of metals have different effects on the environment depending on the nature of the mixture. Hard chrome and molybdenum alloys plating of gun barrels release these metals on firing rounds and transport of these aerosol particles to different environmental conditions causes a health hazard. Number of papers on chromium speciation analysis has significantly increased in recent years because of the wide spread contamination of environment due to industrial, fungicides, magnetic tapes and metallurgy.

Various reagents have been used for the extraction, separation and determination of chromium [5–15], molybdenum [16–20] and tungsten [21–25]; however, these methods are tedious, time consuming, non specific and difficult to separate sequentially chromium, molybdenum and tungsten from each other. Recently, macrocyclic compounds like crown ethers and calixarenes are reported for the chromatographic separation of chromium [26].

On the other hand, atomic spectroscopic method (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES) and ICP-Mass spectrometry do not distinguish Cr(III) and Cr(VI) but gives the total concentration. Dicyclo 18-crown-6 is reported for the extraction of molybdenum and tungsten as thiocyanates [27–29]. However, no systematic studies for their separation are reported.

Calix-crown ethers [30] are the new class of ligands having the binding properties towards alkali and alkaline metals, which can be tuned by the subtle conformation changes around the binding region. Hydroxamic acids are the versatile analytical reagents for the estimation and separation of metals [31–38]. The introduction of the hydroxamic acid group in to the macrocycles may enhance the complexing ability towards the metal ions. With this in a view, in the present investigation, new functionalized calix-crown ether with hydroxamic acid group (Fig. 1) is synthesized and used for the complexation, liquid–liquid extraction, speciation and sequential separation of Cr(III), Mo(VI) and W(VI) from solid wastes. The present extraction method removes the bulk of the major elements and at the same time, concentrates the desired metal species into a small volume of the solution. The chloroform extract is directly inserted into plasma, which produces a 30-fold increase in sensitivity and detection limit.

2. Experimental

2.1. Chemicals

All the chemicals and solvents used were of analytical grade and from E. Merck unless otherwise specified.

2.2. Reagents

Stock solution (1.68×10^{-3} M, 0.2%) of calix-crown hydroxamic acid was prepared in $CHCl_3$.

2.3. Apparatus

The CIBA corning glass vessels were used. Electronic spectra were recorded on a CIBA-Corning 2800 UV–visible spectrophotometer with matching 10 mm quartz cells, pH measurements were performed with Systronic pH meter Model 335, equipped with a combined glass and calomel electrode.

Plasma Scan Model 710 Sequential plasma, Inductively Coupled Atomic Emission Spectrophotometer with plasma Scan multitasking computer and peristaltic pump was used. The following conditions were set for ICP-AES, Ref 27.12 M HZ, incidental power 2000 W, GMK nebulizer, Sample concentration 1.0 ng mL^{-1}, RF power 5 W, observation height 14 mm, argon coolant flow 13 L min^{-1}, wavelength set for chromium 262.72 nm, for molybdenum 202.30 nm and for tungsten 207.91 nm.

2.4. Metal solutions

Standard solutions of Cr(III), Mo(VI) and W(VI) were prepared by dissolving 3.83 g of $CrCl_3·6H_2O$ in 250 mL of water, 1.79 g of $(NH_4)_6Mo_7O_{24}·4H_2O$ in 100 mL of water and 1.84 g of $Na_2WO_4·2H_2O$ in 250 mL of water. Final concentrations were determined spectrophotometrically [9,14,15,17,36].

2.5. Extraction procedure

An aliquot of sample solution containing 98.2–196.2 μg of Cr(III), 99–198 μg of Mo(VI) or 99–199 μg of W(VI) was transferred in to 25 mL separator funnel and pH or molarity of the HCl solution was adjusted [for Cr(III) pH 4.5, Mo(VI) 1.5 M HCl and for W(VI) 6.0 M HCl] with buffer or conc. HCl. The mixture was then shaken with 5.0 mL (0.2%) chloroform solution of calix-crown hydroxamic acid for 5 min. The organic layer was separated, dried over anhydrous sodium sulfate and transferred to 10.0 mL volumetric flask. The organic layer was made up to 10.0 mL with

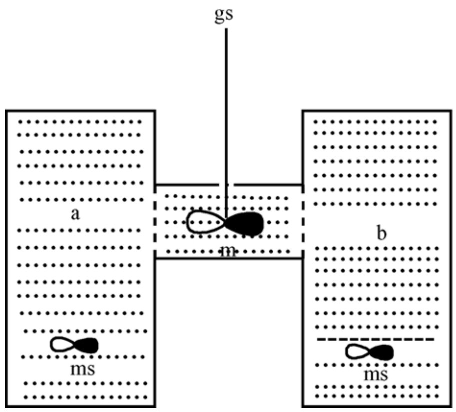

Fig. 2. Membrane cell for the 13,25,31-calix[6]crown hydroxamic transport of Cr, Mo and W acid; a, feed solution; b, received; phase (stirred); m, membrane; ms, magnetic stirrer; gs, glass stirrer.

chloroform and absorbance was measured against reagent blank.

2.6. Transport condition

The transport conditions were performed with two-glass half diffusion cell, which were separated by the membrane 16 cm^2 (Fig. 2). The membrane was impregnated with carrier calix-crown hydroxamic acid dissolved in chloroform and fixed between the half-cell. In support of this liquid membrane transport experiments the samples were taken from the fixed and receiving solutions at scheduled time intervals and analyzed for the Cr, Mo and W by spectrophotometry and ICP-AES.

3. Results and discussion

The chloroform extract of calix-crown hydroxamic acid complexes of chromium(III), molybdenum(VI) and tungsten(VI) have the maximum absorbances at 387, 410 and 320 nm, respectively with molar absorptivity 1.38×10^4, 2.24×10^4 and 1.99×10^4 L mol^{-1} cm^{-1} for Cr(III), Mo(VI) and W(VI), respectively. The reagent blank does not absorb at these wavelength. Under the optimum conditions, the calibration curves are linear over the concentration range of 0.98–13.70 μg mL^{-1} for Cr(III), 0.99–14.98 μg mL^{-1} for Mo(VI) and 0.99–15.68 μg mL^{-1} for W(VI). The linear equations with the regressions are as follows: Cr(III), Conc. = 11.1 × Absorbance with $r = 0.999$; Mo(VI), Conc. = 3.5 × Absorbance with $r = 0.999$; and W(VI), Conc. = 3.1 × Absorbance with $r = 0.999$. Ten determinations of each 15 μg mL^{-1} of Cr(III), Mo(VI) and W(VI) solutions gave a relative standard deviation of 2.3, 2.8 and 3.0%, respectively. For ICP-AES measurements the extract is directly inserted in to the plasma through peristaltic pump, which increases the sensitivity with the detection limits 3 ng mL^{-1}.

Table 1
Thermodynamic function for the extraction of Cr, Mo and W, calix-crown hydroxamic acid

Temperature (K)	Cr(III)-calix-crown HA				Mo(VI)-calix-crown HA				W(VI)-calix-crown HA			
	K_{ex}	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J K^{-1})	K_{ex}	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J K^{-1})	K_{ex}	ΔG^0 (kJ/mol)	ΔH^0 (kJ/Mol)	ΔS^0 (J K^{-1})
288	7.40×10^{-4}	–	–	–	5.10×10^{-8}	–	–	–	2.70×10^{-8}	–	–	–
298	7.51×10^{-4}	−85.26	−42.76	138	5.15×10^{-8}	−93.10	−46.62	156	2.78×10^{-8}	−97.79	−48.92	164
308	7.58×10^{-4}	−87.16	−43.60	137	5.25×10^{-8}	−96.84	−48.80	158	2.89×10^{-8}	−99.99	−49.61	161
318	7.65×10^{-4}	−86.29	−43.82	138	5.36×10^{-8}	−103.14	−51.63	162	2.94×10^{-8}	−104.62	−58.31	164

3.1. Effect of pH/M HCl and time

Cr(III), Mo(VI) and W(VI) were extracted with calix-crown hydroxamic acid at different pH/M HCl. It was observed that maximum extraction (%*E*) and K_d was found for Cr(III) at pH 4.5, Kd 1380, Mo(VI) with 1.5 M HCl K_d 1460 and for W(VI) with 6.0 M HCl and K_d 985, (Table 1). It was found that 5 min of shaking time is sufficient for the quantitative extraction of Cr(III), Mo(VI) and W(VI).

3.2. Effect of concentration of calix-crown hydroxamic acid

The influence of the concentration of calix-crown hydroxamic acid was studied by extracting a fixed amount of Cr(III), Mo(VI) or W(VI) with varying concentration of calix-crown hydroxamic acid. It was found that a 10.0 mL aliquot of 1.68×10^{-3} M calix-crown hydroxamic acid was adequate for the complete extraction of Cr(III), Mo(VI) and W(VI). However, excess of the reagent does not effect the extraction (%*E*).

3.3. Choice of extracting solvent

Among chloroform, dichloromethane, benzene, toluene and iso-amyl alcohol, chloroform was found to be the most suitable solvent for the quantitative extraction of chromium, molybdenum and tungsten (Table 2).

3.4. Effect of temperature

The thermodynamic parameters for chromium, molybdenum and tungsten complexes were determined at various temperatures between 288 and 318 K (Table 3). Results show that with the increase in the temperature, extraction constant increases. The plot of log K_{ex} against 100/*T* is linear. The negative values of free energy show that the reaction is exothermic and favourable for extraction.

3.5. Stoichiometry of the complex

The stoichiometry of the complexes was established by plotting the graph of logarithm of metal distribution ratio

Table 2
Effect of interfering ions on the extraction of chromium

Diverse ions	Added as	Milligrams added	Log $K^n{}_M{}^+$	K_{Cr}	Found (μg mL^{-1})	
					Spectroph.	ICP-AES
Cr	–	50	11.32	1.00	4.98 ± 0.05	4.997 ± 0.006
Ag^+	$AgNO_3$	50	0.32	$10^{11.00}$	4.97 ± 0.05	4.996 ± 0.008
Ca^{2+}	$CaCl_2$	80	0.35	$10^{10.97}$	4.99 ± 0.03	5.005 ± 0.006
Zn^{2+}	$ZnSO_4$	60	1.15	$10^{10.17}$	5.02 ± 0.05	4.999 ± 0.005
Co^{2+}	$Co(NO_3)_2$	60	1.21	$10^{10.11}$	5.03 ± 0.05	5.005 ± 0.008
Ni^{2+}	$NiCl_2$	60	1.25	$10^{10.07}$	4.98 ± 0.05	5.002 ± 0.005
Mn^{2+}	$MnCl_2$	60	1.30	$10^{10.02}$	4.97 ± 0.06	5.008 ± 0.009
Cu^{2+}	$CuCl_2$	60	1.28	$10^{10.04}$	5.04 ± 0.04	4.998 ± 0.005
Mg^{2+}	$MgSO_4$	80	0.95	$10^{10.37}$	4.99 ± 0.03	5.002 ± 0.006
Hg^{2+}	$Hg(NO_3)_2$	50	0.80	$10^{10.52}$	5.00 ± 0.03	4.997 ± 0.007
Pb^{2+}	$Pb(NO_3)_2$	50	0.90	$10^{10.42}$	5.03 ± 0.05	4.996 ± 0.008
Sn^{2+}	$SnCl_2$	50	0.90	$10^{10.42}$	5.01 ± 0.03	4.999 ± 0.005
Al^{3+}	$AlCl_3$	80	1.10	$10^{10.22}$	4.98 ± 0.05	5.008 ± 0.009
Fe^{3+}	$FeCl_3$	60	2.10	$10^{9.22}$	4.97 ± 0.06	5.00 ± 0.005
As^{3+}	As_2O_3	70	1.19	$10^{10.13}$	4.99 ± 0.03	5.002 ± 0.005
Sb^{3+}	$SbCl_3$	60	1.25	$10^{10.07}$	4.99 ± 0.03	5.052 ± 0.007
Bi^{3+}	$BiCl_3$	60	1.30	$10^{10.02}$	4.99 ± 0.03	4.996 ± 0.008
Sc^{3+}	$ScCl_3$	70	1.10	$10^{10.22}$	5.02 ± 0.04	4.997 ± 0.006
Sr^{2+}	$SrCl_2$	80	1.00	$10^{10.32}$	5.00 ± 0.04	4.995 ± 0.007
Ba^{2+}	$BaCl_2$	80	0.93	$10^{10.39}$	5.02 ± 0.03	4.996 ± 0.007
Ga^{3+}	$GaCl_3$	80	0.88	$10^{10.49}$	5.04 ± 0.06	4.993 ± 0.007
In^{3+}	$InCl_3$	80	0.85	$10^{10.47}$	4.97 ± 0.05	4.998 ± 0.005
Ce^{4+}	$Ce(SO_4)_2$	60	2.20	$10^{9.12}$	4.97 ± 0.05	5.008 ± 0.008
Th^{4+}	$Th(NO_3)_4$	50	2.30	$10^{9.02}$	5.03 ± 0.04	4.995 ± 0.007
U^{6+}	$UO_2(NO_3)_2$	50	2.40	$10^{8.92}$	5.02 ± 0.05	4.994 ± 0.008
Gd^{3+}	$Gd(NO_3)_3$	50	2.05	$10^{9.27}$	4.98 ± 0.05	4.998 ± 0.005
Pr^{3+}	$Pr(NO_3)_3$	50	1.85	$10^{10.47}$	4.97 ± 0.04	4.996 ± 0.005
Nd^{3+}	$Nd(NO_3)_3$	50	1.65	$10^{10.47}$	4.97 ± 0.04	4.996 ± 0.005
V^{5+}	NH_4VO_3	50	2.65	$10^{9.67}$	5.05 ± 0.06	4.996 ± 0.007
Mo	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	60	0.45	$10^{10.85}$	5.00 ± 0.04	4.995 ± 0.007
W	$Na_2WO_4\cdot 2H_2O$	60	0.32	$10^{11.00}$	5.04 ± 0.06	4.993 ± 0.007
Cl^-	NH_4Cl	80	0.70	$10^{10.52}$	5.01 ± 0.03	5.003 ± 0.008
$NO_3{}^-$	NH_4NO_3	80	0.60	$10^{10.72}$	5.02 ± 0.03	5.003 ± 0.005
F^-	NH_4F	80	0.65	$10^{10.67}$	5.01 ± 0.03	5.004 ± 0.007
$SO_4{}^{2-}$	$(NH_4)_2SO_4$	80	0.50	$10^{10.82}$	4.99 ± 0.02	4.999 ± 0.005

Chromium, 5.0 μg mL^{-1}; pH, 4.5 log; solvent, chloroform.

Table 3
Effect of interfering ions on the extraction of molybdenum

Diverse ions	Added as	Milligrams added	Log $K^{n}{}_{\mathrm{M}^{+}}$	K_{Mo}	Found (μgmL^{-1})	
					Spectroph.	ICP-AES
Mo	–	50	14.05	1.00	4.97 ± 0.04	4.995 ± 0.006
Ag^+	$AgNO_3$	50	0.85	$10^{13.00}$	4.99 ± 0.04	4.997 ± 0.005
Ca^{2+}	$CaCl_2$	80	0.65	$10^{13.40}$	5.02 ± 0.03	5.002 ± 0.002
Zn^{2+}	$ZnSO_4$	60	1.10	$10^{12.45}$	4.98 ± 0.05	4.999 ± 0.005
Co^{2+}	$Co(NO_3)_2$	60	1.20	$10^{12.85}$	5.03 ± 0.05	5.005 ± 0.008
Ni^{2+}	$NiCl_2$	60	1.35	$10^{12.70}$	4.96 ± 0.05	5.004 ± 0.002
Mn^{2+}	$MnCl_2$	60	1.20	$10^{12.85}$	4.99 ± 0.04	5.004 ± 0.008
Cu^{2+}	$CuCl_2$	60	1.50	$10^{12.55}$	5.05 ± 0.05	4.997 ± 0.004
Mg^{2+}	$MgSO_4$	80	0.80	$10^{12.25}$	5.05 ± 0.04	5.001 ± 0.002
Hg^{2+}	$Hg(NO_3)_2$	50	0.70	$10^{12.35}$	4.99 ± 0.03	4.998 ± 0.005
Pb^{2+}	$Pb(NO_3)_2$	50	0.95	$10^{12.15}$	5.05 ± 0.04	4.997 ± 0.005
Sn^{2+}	$SnCl_2$	50	0.65	$10^{12.30}$	4.98 ± 0.03	4.997 ± 0.004
Al^{3+}	$AlCl_3$	80	0.55	$10^{12.50}$	4.99 ± 0.05	5.005 ± 0.009
Fe^{3+}	$FeCl_3$	60	2.00	$10^{12.05}$	4.99 ± 0.06	5.01 ± 0.004
As^{3+}	As_2O_3	70	1.15	$10^{12.90}$	4.99 ± 0.03	5.002 ± 0.005
Sb^{3+}	$SbCl_3$	60	1.05	$10^{13.00}$	4.98 ± 0.06	5.05 ± 0.004
Bi^{3+}	$BiCl_3$	60	0.95	$10^{13.20}$	5.05 ± 0.03	4.998 ± 0.008
Sc^{3+}	$ScCl_3$	70	1.00	$10^{13.05}$	4.99 ± 0.04	4.999 ± 0.006
Sr^{2+}	$SrCl_2$	80	0.85	$10^{13.20}$	5.00 ± 0.04	4.995 ± 0.007
Ba^{2+}	$BaCl_2$	80	0.55	$10^{13.50}$	5.04 ± 0.03	4.998 ± 0.007
Ga^{3+}	$GaCl_3$	80	0.65	$10^{13.40}$	4.99 ± 0.05	4.983 ± 0.008
In^{3+}	$InCl_3$	80	0.70	$10^{12.90}$	4.99 ± 0.05	4.999 ± 0.005
Ce^{4+}	$Ce(SO_4)_2$	60	1.20	$10^{9.12}$	4.98 ± 0.05	5.007 ± 0.008
Th^{4+}	$Th(NO_3)_4$	50	1.25	$10^{12.95}$	4.99 ± 0.08	4.997 ± 0.05
U^{6+}	$UO_2(NO_3)_2$	50	1.30	$10^{18.80}$	5.05 ± 0.02	4.984 ± 0.007
Gd^{3+}	$Gd(NO_3)_3$	50	0.95	$10^{13.10}$	4.99 ± 0.05	4.978 ± 0.005
Pr^{3+}	$Pr(NO_3)_3$	50	0.85	$10^{13.20}$	4.98 ± 0.04	4.998 ± 0.005
Nd^{3+}	$Nd(NO_3)_3$	50	0.70	$10^{13.85}$	4.99 ± 0.04	4.986 ± 0.005
V^{5+}	NH_4VO_3	50	2.80	$10^{11.25}$	5.02 ± 0.05	4.998 ± 0.005
Cr	$CrCl_3{\cdot}6H_2O$	60	0.25	$10^{13.80}$	5.02 ± 0.05	4.998 ± 0.005
W	$Na_2WO_4{\cdot}2H_2O$	60	1.65	$10^{12.40}$	5.05 ± 0.06	4.992 ± 0.005
Cl^-	NH_4Cl	80	0.50	$10^{13.55}$	4.99 ± 0.05	5.004 ± 0.004
$NO_3{}^-$	NH_4NO_3	80	0.50	$10^{13.55}$	5.05 ± 0.04	5.004 ± 0.003
F^-	NH_4F	80	0.45	$10^{13.60}$	5.02 ± 0.05	5.001 ± 0.087
$SO_4{}^{2-}$	$(NH_4)_2SO_4$	80	0.50	$10^{13.55}$	4.98 ± 0.04	4.989 ± 0.004
La^{3+}	$La(NO_3)_3$	80	0.70	$10^{10.55}$	5.02 ± 0.03	4.998 ± 0.007

Molybdenum, 5.0 μg mL^{-1}; HCl, 1.5 M; solvent, chloroform.

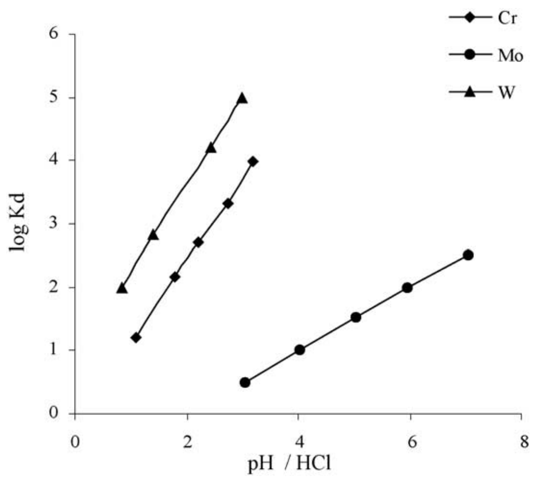

Fig. 3. log K_d vs. pH.

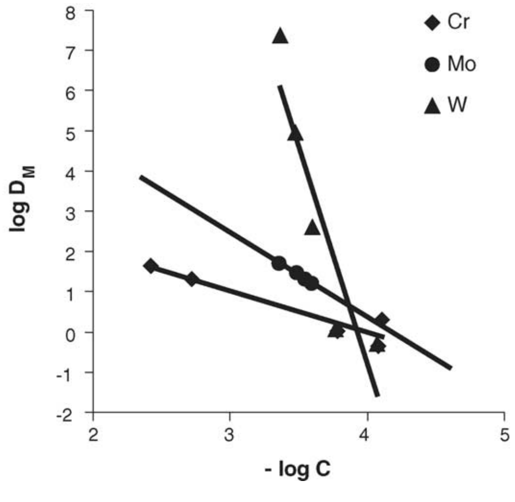

Fig. 4. $-\log C$ vs. $\log D_M$.

Table 4
Effect of interfering ions on the extraction of tungsten

Diverse ions	Added as	Milligrams added	Log $K^{n}{}_{\mathrm{M}}{}^{+}$	K_{W}	Found (μg mL^{-1})	
					Spectroph.	ICP-AES
W	–	50	14.89	1.00	4.98 ± 0.04	4.997 ± 0.006
Ag^{+}	$AgNO_3$	50	0.70	$10^{14.19}$	4.98 ± 0.06	4.998 ± 0.004
Ca^{2+}	$CaCl_2$	80	0.65	$10^{14.24}$	5.05 ± 0.03	5.004 ± 0.002
Zn^{2+}	$ZnSO_4$	60	0.95	$10^{13.14}$	4.99 ± 0.05	4.998 ± 0.005
Co^{2+}	$Co(NO_3)_2$	60	1.08	$10^{13.81}$	5.05 ± 0.04	5.005 ± 0.008
Ni^{2+}	$NiCl_2$	60	1.21	$10^{13.68}$	4.99 ± 0.05	5.02 ± 0.006
Mn^{2+}	$MnCl_2$	60	1.23	$10^{13.66}$	4.98 ± 0.04	5.005 ± 0.008
Cu^{2+}	$CuCl_2$	60	1.45	$10^{13.45}$	5.04 ± 0.05	4.998 ± 0.004
Mg^{2+}	$MgSO_4$	80	1.00	$10^{13.89}$	4.99 ± 0.04	5.002 ± 0.002
Hg^{2+}	$Hg(NO_3)_2$	50	0.82	$10^{14.07}$	4.98 ± 0.04	4.999 ± 0.005
Pb^{2+}	$Pb(NO_3)_2$	50	1.05	$10^{13.84}$	4.99 ± 0.04	4.998 ± 0.005
Sn^{2+}	$SnCl_2$	50	0.65	$10^{13.13}$	4.99 ± 0.03	4.998 ± 0.004
Al^{3+}	$AlCl_3$	80	0.55	$10^{13.15}$	5.02 ± 0.05	5.002 ± 0.009
Fe^{3+}	$FeCl_3$	60	2.00	$10^{13.59}$	4.98 ± 0.06	5.04 ± 0.004
As^{3+}	As_2O_3	70	1.15	$10^{13.14}$	4.98 ± 0.03	5.002 ± 0.005
Sb^{3+}	$SbCl_3$	60	1.05	$10^{13.04}$	4.99 ± 0.06	5.04 ± 0.004
Bi^{3+}	$BiCl_3$	60	0.95	$10^{13.07}$	5.02 ± 0.03	4.999 ± 0.008
Sc^{3+}	$ScCl_3$	70	1.00	$10^{13.09}$	4.98 ± 0.04	4.997 ± 0.006
Sr^{2+}	$SrCl_2$	80	0.85	$10^{13.41}$	5.02 ± 0.04	4.999 ± 0.007
Ba^{2+}	$BaCl_2$	80	0.55	$10^{13.43}$	5.01 ± 0.03	4.997 ± 0.007
Ga^{3+}	$GaCl_3$	80	0.65	$10^{14.11}$	4.98 ± 0.05	4.987 ± 0.004
In^{3+}	$InCl_3$	80	0.70	$10^{14.26}$	4.98 ± 0.06	4.999 ± 0.002
Ce^{4+}	$Ce(SO_4)_2$	60	1.20	$10^{13.21}$	4.99 ± 0.05	5.004 ± 0.007
Th^{4+}	$Th(NO_3)_4$	50	1.25	$10^{12.94}$	4.98 ± 0.08	4.997 ± 0.05
U^{6+}	$UO_2(NO_3)_2$	50	1.30	$10^{12.88}$	5.04 ± 0.02	4.994 ± 0.007
Gd^{3+}	$Gd(NO_3)_3$	50	0.95	$10^{13.04}$	4.99 ± 0.05	4.988 ± 0.005
Pr^{3+}	$Pr(NO_3)_3$	50	0.85	$10^{13.29}$	5.02 ± 0.04	5.05 ± 0.005
Nd^{3+}	$Nd(NO_3)_3$	50	0.70	$10^{13.24}$	4.98 ± 0.04	4.989 ± 0.005
V^{5+}	NH_4VO_3	50	2.80	$10^{12.84}$	5.05 ± 0.05	5.02 ± 0.005
Cr	$CrCl_3{\cdot}6H_2O$	60	0.69	$10^{14.20}$	4.99 ± 0.04	4.986 ± 0.006
Mo	$Na_2WO_4{\cdot}2H_2O$	60	1.95	$10^{12.94}$	4.98 ± 0.04	4.995 ± 0.007
Cl^{-}	NH_4Cl	80	0.50	$10^{14.39}$	5.02 ± 0.05	5.002 ± 0.004
$NO_3{}^{-}$	NH_4NO_3	80	0.50	$10^{14.39}$	5.04 ± 0.04	5.002 ± 0.003
F^{-}	NH_4F	80	0.45	$10^{14.39}$	4.99 ± 0.05	5.001 ± 0.087
$SO_4{}^{2-}$	$(NH_4)_2SO_4$	80	0.50	$10^{14.24}$	4.99 ± 0.04	4.999 ± 0.004
La^{3+}	$La(NO_3)_3$	80	0.70	$10^{14.50}$	5.05 ± 0.03	5.02 ± 0.007

Tungsten, 5.0 μg mL^{-1}; HCl, 6.0 M; solvent, chloroform.

($\log D_{\mathrm{M}}$) against the negative logarithm of the concentration of ligand ($-\log C$) and $\log K_{\mathrm{d}}$ against pH, which shows the formation of 1:1 metal: calix-crown hydroxamic acid complex with a slope 1.00 (Figs. 3 and 4). The extraction was carried out by taking a fixed amount of Cr(III), Mo(VI and W(VI) with varying concentration of calix-crown hydroxamic acid. This confirms that one molecule of ligand is required for 1 mol of metal ion and the expected structure of the complex can be of the type:

The extraction of Cr(III), Mo(VI) and W(VI) with calix-crown hydroxamic acid can be represented as,

$$\mathrm{CrCl}_{3[\mathrm{aq}]} + \mathrm{H}_2\mathrm{A}_{[\mathrm{org}]} \rightleftharpoons [\mathrm{Cr}-\mathrm{A}]\mathrm{Cl}_{[\mathrm{org}]} + 2[\mathrm{H}^{+}]_{[\mathrm{aq}]} \qquad (1)$$

$$[\mathrm{MoO}_2]_{[\mathrm{aq}]}{}^{2+} + [\mathrm{H}_2\mathrm{A}]_{[\mathrm{org}]} \rightleftharpoons [\mathrm{MoO}_2-\mathrm{A}]_{[\mathrm{org}]} + 2[\mathrm{H}^{+}]_{[\mathrm{aq}]} \qquad (2)$$

$$[\mathrm{WO}_2]_{[\mathrm{aq}]}{}^{2+} + [\mathrm{H}_2\mathrm{A}]_{[\mathrm{org}]} \rightleftharpoons [\mathrm{WO}_2-\mathrm{A}]_{[\mathrm{org}]} + 2[\mathrm{H}]_{[\mathrm{aq}]}{}^{+} \qquad (3)$$

Table 5
Determination of chromium(III) and chromium(VI) in tannery effluents

Synthetic sample (ppm) Cr(III) + Cr(VI)	Chromium total Cr(III) + Cr(VI) (μg)	Concentration of Cr(III) (μg)	Concentration of Cr(VI) (μg)
100 + 100	199.40	99.90	99.50
0.5 + 0.0	0.50 ± 0.03	0.50	0.00
40.0 + 5.0	45.0 ± 0.04	40.02	4.9
5.0 + 40.0	45.0 ± 0.03	4.85	40.15
1.5 + 0.50	2.1 ± 0.02	1.49	0.52
Chromic plating rinsing water sample	280.0 ± 0.05	9.00	271.00

Table 6
Determination of Cr(III), Mo(VI) and W(VI) in silicate rock, ores, alloys and steel samples

Sample	Cr(III) (ppm)		Mo(VI) (ppm)		W(VI) (ppm)	
	Certified	Found	Certified	Found	Certified	Found
Basalt USGS BCR-1	15.00	14.92	1.20	1.18	0.50	0.53
Basalt GIT: BE-N	360.00	359.92	–	–	29.00	28.90
Basalt CRPG: BR	380.00	379.91	4.10	3.94	29.00	28.95
Chromite $FeCr_2O_4$	9.8%	9.782%	–	–	–	–
Molybdenite MoS_2	–	–	59.94%	59.52%	–	–
Wolframite $[Fe(Mn)WO_4]$	–	–	–	–	47.67%	47.51%
GKW Steel, India	1.02%	1.018%	10.50	10.45	2.50	2.48
Stainless steel no.304	18.0 %	17.98 %	25.80	25.50	3.00	2.50
BCS 406/1	6.50	6.55	1.0%	0.92%	3.50	3.48
BCS 219/4	5.10	4.98	0.58%	0.56%	1.50	1.55
BCS 261/1	8.55	8.50	0.11%	0.10%	4.75	4.73

where the extraction constant K_{ex} can be given

$$K_{ex} = \frac{[M - A]_{[org]} \times [H^+]_{[aq]}}{[M]_{[aq]}{}^{n+} \times [H_2A]_{[org]}} \qquad (4)$$

where A stands for the hydroxamate anion of calix-crown hydroxamic acid.

D_M is metal distribution ratio between organic and aqueous phases given as,

$$D_M = \frac{[M - A]_{[org]}}{[M]_{[aq]}{}^{n+}} \qquad (5)$$

where the subscripts [aq] and [org] are aqueous and organic phases, respectively.

The general extraction constant K_{ex} is given as,

$$K_{ex} = \frac{D_M[H^+]_{[aq]}{}^2}{[HA]_{[org]}} \qquad (6)$$

So,

$$\log K_{ex} = \log D_M - 2\,pH - 2\,\log[HA] \qquad (7)$$

The two-phase stability constants (β_2, K'_e) of the complexes can be given as,

$$\log(\beta_2, K'_e) = \log K_{ex} + 2\,pK_a + 2\,\log K_e \qquad (8)$$

where (β_2, K'_e) and K_{ex} are the respective stability and extraction constants of the chelate.

3.6. Effect of interfering ions

In order to examine the utility of the present method, the effect of various cations and anions in the separation and determination of chromium, molybdenum and tungsten was studied. Interference studies were performed by measuring the absorbance of the extracted organic phase and also by

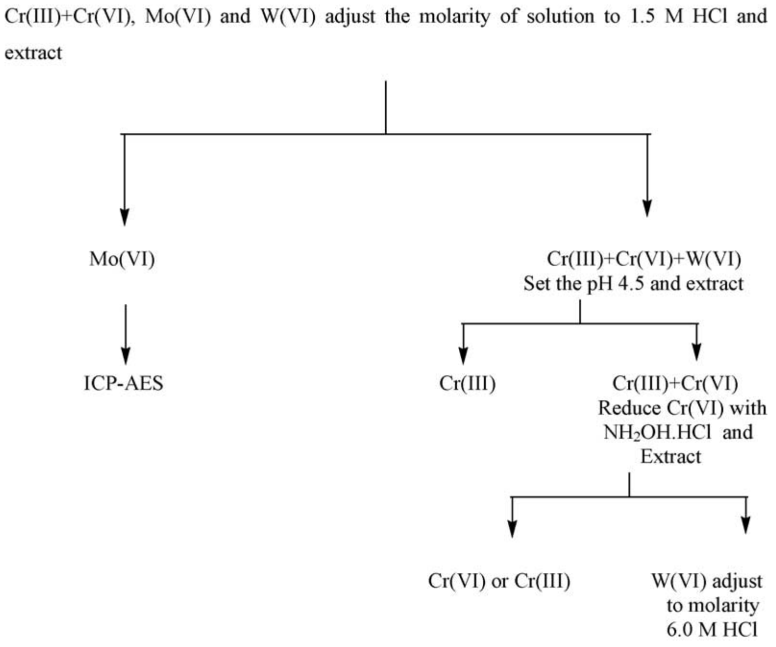

Fig. 5. Sequential separation of chromium(III), molybdenum(VI) and tungsten(VI).

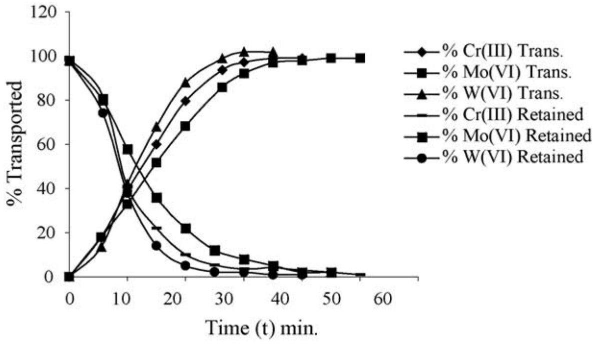

Fig. 6. Transportation of Cr(III), Mo(VI) and W(VI) with calix-crown hydroxamic acid.

ICP-AES of both the extract as well as aqueous phase. The tolerance limit was set as the amount of foreign ion causing a change of absorbance of 0.02 on absorbance or 2% error in the recovery of Cr, Mo and W.

Chromium, molybdenum and tungsten were extracted in presence of large number of competitive ions at the optimum pH/molarity of HCl and none of them affected the absorbance of chromium, molybdenum and tungsten (Tables 4–6). This shows that log (β_2, K_e) values are greater than competing metal cations ($K^n{}_{M^+}$) and anions ($K^n{}_{A^-}$), which were determined independently at pH 4.5, 1.5 M HCl and 6.0 M HCl for chromium, molybdenum and tungsten, respectively. The results obtained show that selectivity factor ($K_{Cr} = \beta_2 K_e / K^n{}_{M^+}$) or ($\beta_2 K_e / K^n{}_{A^-}$) for chromium complex K_{Cr}, molybdenum K_{Mo} or tungsten K_W has a high selectivity with most of the cations and anions. The moderate amount of commonly metal ions associated with chromium, molybdenum and tungsten were tolerated. The sequential separation of Cr, Mo and W is shown in Fig. 5.

3.7. Limits of preconcentration and preconcentration factor

One liter of aqueous phase containing 5 μg of chromium, molybdenum and tungsten was divided in 10 portions of 100 mL each. Extraction was performed using 20 mL of chromium solution of PCCCHA, which was successively added to individual portion of the aqueous phase sample so that the chromium, molybdenum or tungsten became concentrated in 20 mL of organic solvent. Determinations were made by ICP-AES.

For evaluation of the efficiency of preconcentration, expressed in recovery, the concentration of metal (Cr, Mo or W) in organic phase and the remaining in aqueous phase was measured by ICP-AES against a calibration standard solution in chloroform. The recovery (R%) was calculated from the equation, $R\% = [(A_{stand} - A_S)/A_{std}] \times 100$, where, A_{stand} is the absorbance value for the sample containing a known amount of Cr, Mo or W added to the sample solution prior to extraction, A_{std} is the absorbance value for the standard Cr, Mo or W in chloroform with the same analyte concentration on the standard addition, and A_S is the absorbance value of the sample. The quantitative collection of chromium, molybdenum and tungsten was possible with recovery 99.9 ± 0.35, 99.7 ± 0.4 and 99.9 ± 0.5%, respectively. The concentration factors were 111, 115 and 107 for chromium, molybdenum and tungsten.

Table 7
Determination of Cr(III), Mo(VI) and W(VI) in food, pharmaceutical and biological samples

Sample	Found ($\mu g\,L^{-1}$)		
	Cr(III)	Mo(VI)	W(VI)
Green beans	9.6	0.85	0.10
White cabbage	7.2	1.2	0.10
Coffee	5.8	1.3	0.02
Tea leaves	6.2	1.5	0.01
Radishes	4.8	1.1	0.24
Tape water	0.20	0.24	0.02
Sea water	3.50	0.8	0.10
Chromium plating, rinsing water	6000	3.5	0.25
Kelp	0.08	0.50	0.01
Murg bean	0.05	0.30	0.02
Pork liver	0.03	0.20	0.01
Urine	0.18 (0.20)	1.21 (1.20)	0.03 (0.05)
Blood	2.92 (2.90)	3.63 (3.70)	0.03 (0.03)
Serum	2.11 (2.10)	5.28 (5.30)	0.07 (0.08)
	($mg\,Kg^{-1}$)		
Optisulin	0.497 (0.500)	0.080	0.005
Fourts B	0.148 (0.150)	0.060	0.008
Chromoplex	0.197 (0.200)	0.050	0.006

The standard samples are from Analytical USA and values given in parenthesis.

3.8. Kinetics of transportation of Cr(III), Mo(VI) and W(VI) for their sequential separation

Transport experiments were performed by taking Cr(III), Mo(VI) and W(VI) (1×10^{-4} M) concentration in appropriate pH or molarity of HCl as source phase, 0.05 M HCl as receiving phase and 1×10^{-3} M and calix-crown hydroxamic acid as a carrier. Concentrations of Cr, Mo and W in the aqueous compartment were monitored as a function of time by spectrophotometry and ICP-AES. The transport data are the average of at least four runs whose experimental error is less than 3.0%. No movement of metal ions was observed unless a carrier calix-crown hydroxamic acid was

Table 8
Determination of Cr(III), Mo(VI) and W(VI) in natural water, soil, effluent

Sample	Cr(III)	Mo(VI)	W(VI)
Natural water ($\mu g\,mL^{-1}$)	1.98 ± 0.02	0.08 ± 0.01	0.02 ± 0.01
Soil sample ($mg\,Kg^{-1}$)			
I	1.98	0.035 ± 0.03	0.22 ± 0.05
II	3.96	0.45 ± 0.05	0.18 ± 0.05
Effluent ($\mu g\,mL^{-1}$)	20.08 ± 0.05	362.45 ± 0.08	44.02 ± 0.05

Effluents samples were obtained from GIDC Vatva, Ahmedabad.

used. The transport of metal ions is of psuedounimetal reaction of the first order. It has been observed that maximum transport is observed till 35 min with $t_{1/2} = 12$ min, $K = 5.7 \times 10^{-2}$ mol^{-1} min^{-1} for Cr(III); 45 min with $t_{1/2} = 15$ min, $K = 4.6 \times 10^{-2}$ mol^{-1} min^{-1} for Mo(VI); and 30 min, with $t_{1/2} = 11$ min, $K = 6.3 \times 10^{-2}$ mol^{-1} min^{-1} for W(VI). The Cr, Mo and W transport and retention with time is shown in Fig. 6.

3.9. Speciation of chromium(III) and chromium(VI)

A portion of tannery effluent (100 mL) containing 200 μg of total chromium [Cr(III) and Cr(VI)] was reduced to chromium(III) with hydroxylamine hydrochloride. Then the Cr(III) was extracted as total Cr(III). The Cr(III) was directly extracted and the amount of Cr(VI) was obtained by subtracting the Cr(III) contents from total Cr content. The results are given in (Table 7).

3.10. Performance characteristic in the analysis of the standard samples, biological and environmental samples

To check the validity of the proposed method, chromium, molybdenum and tungsten were determined in standard steel alloys, geological and soil, food and water samples. The results obtained are in good agreement with the certified values (Table 8).

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References

[1] S.J. Lipard, J.M. Berg, Principles of Bioinorganic Chemistry, Panima publishing Corp., New Delhi, 1995, p. 103.
[2] J.O. Niriagu, E. Nieboa, Chromium in Natural and Human Environments, Wiley, New York, 1988.
[3] T.M. Florenic, G.E. Bately, CRC Int. Rev. Anal. Chem. 9 (1980) 219.
[4] R. Conelis, in: R.F. Mherber, M. Stoeppler (Eds.), Trace element Analysis in Biological Specimors, Elsevier, The Netherlands, 1994.
[5] H.D. Revanasiddappa, T.N. Kiran Kumar, Talanta 60 (2003) 1.
[6] M.D. Lanagan, D.C. Ibana, Mineral Eng. 16 (2003) 237.
[7] D.D. Dhadke, P.M. Dhadke, S.M. Khopkar, Indian J. Chem. Sect. A 38 (1999) 1079.
[8] K. Satoshi, Bull. Chem. Soc. Jpn. 73 (2000) 1175.
[9] X.-F. Chen, Y.-Z. Zhang, Henon Huagong 6 (2002) 32.
[10] Y.-S. Long, D.-M. Chen, Guanxi Shifan Daxue Xuebao.Ziran Kexue 20 (2002) 61.
[11] B.S. Mohite, S.G. Mni, S.M. Sawant, Chem. Res. Env. Res. 10 (2001) 339.
[12] S. Hirata, Y. Umezaki, M. Ikeda, Anal. Chem. 58 (1986) 2602.
[13] R.R. Greenberg, R. Zeiser, H.M. Kingston, T.M. Sullivan, L Fresenius, Anal. Chem. 332 (1988) 652.
[14] R.E. Shaffer, J.O. Cross, S.L. Rose-Pehesson, W.T. Elam, Anal. Chim. Acta 442 (2001) 295.
[15] C.M. Davidson, R.P. Thomas, S.E. Mcvey, R. Perala, D. Littlejohn, A.M. Ure, Anal. Chim. Acta 291 (1994) 277.
[16] M. Alkan, M. Kharun, F. Chmilenko, Talanta 59 (2003) 605.
[17] A. Khan, A. Rusheed, S. Ahmed, J. Chem. Soc Pakistan 21 (1999) 382.
[18] N. Averdizade, A.Z. Zalov, K.A. Kuliev, T.A. Amrakhov, V.M. Samedova, J. Anal. Chem. 55 (2000) 331.
[19] M. Kamburova, A. Alexandrov, Chem. Anal. 44 (1999) 745.
[20] B. Berhanu, B.S. Chandravanshi, Anal. Lett. 28 (1995) 1681.
[21] J.-R. hui, Fenxi Shiyanshi 19 (2000) 44.
[22] A.D. Barve, V.M. Shinde, Indian J. Chem. Sect. A 33A (1994) 126.
[23] L.I. Avramenko, L.V. Gudzenko, E.S. Zolotovitskaya, T.N. Trubaeva, E.I. Shelikhina, V.P. Antonovich, A.B. Blank, Z. Anal. Khim. 47 (1992) 737.
[24] S. Xinyou, Fenxi Shiyanshi 10 (1991) 24.
[25] L. Shaolin, W. Jingwell, Gaodeng Xuexiao Xuaxue Xuebao 11 (1990) 355.
[26] V.A. Sasyuk, Zh. Anal. Khim. 46 (1991) 741.
[27] B.S. Mohite, J.M. Patel, J. Radioanal. Nucl. Chem. 150 (1991) 207.
[28] R.C. Kalteka, R. Hausbeck, V. Kiran, Talanta 33 (1986) 215.
[29] Y. Azolotov (Ed.), Macrocyclic Compounds in Analytical Chemistry, Wiley-Interscience, New York, 1997.
[30] M.A. Gorbunova, P.V. Bonnsen, N.L. Engle, E. Bazalair, H. Delmau, B.A. Moyer, Tetrahedron Lett. 44 (2003) 5397.
[31] Y.K. Agrawal, Rev. Anal. Chem. 3 (1980) 51.
[32] Y.K. Agrawal, S.A. Patel, Rev. Anal. Chem. 4 (1980) 237.
[33] Y.K. Agrawal, R.K. Jain, Rev. Anal. Chem. 6 (1982) 49.
[34] S.K. Menon, Y.K. Agrawal, Rev. Inorg. Chem. 16 (1996) 1.
[35] Y.K. Agrawal, Fullerenes Nanotubes Carbon Nanostruct. 11 (2003) 135.
[36] Y.K. Agrawal, S.B. Vora, Microchim. Acta 142 (2003) 255.
[37] M. Derocelle, B.M. Meloughlin, C.T. Sharkey, D.J. Fitzgerold, Org. Biomol. Chem. (2003) 850.
[38] S. Li, N. Deng, F. Zheng, Y. Huang, Talanta 60 (2003) 1097.