ADSORBING COLLOID FLOTATION SEPARATION AND POLAROGRAPHIC DETERMINATION OF Mo(VI) IN WATER

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Summary—A method is described for the flotation and determination of Mo(VI) in water at ng/ml levels. Mo(VI) is preconcentrated and separated by adsorbing colloid flotation employing aluminium(III) hydroxide as collector and sodium lauryl sulphate as surfactant at pH 5.3 ± 0.1. The molybdenum content in the froth is estimated by using the catalytic wave of Mo(VI) in the presence of nitrate by charging current compensated d.c. polarography (CCCDCP) or differential pulse polarography (DPP). The effect of variables such as pH, ionic strength, concentration of collector and surfactant, time of stirring and gas flow-rate on the recovery of Mo by flotation is reported. The effects of various cations and anions on the flotation and determination of Mo are studied. This method is employed for the determination of molybdenum in natural fresh water samples.

Adsorbing colloid flotation (ACF) has been applied to the separation and preconcentration of trace elements in many aqueous systems during the past two decades.[1-13] Analytical applications of flotation have been reviewed recently.[14] Adsorbing colloid flotation has some advantages over ion flotation (IF) such as (i) surfactant needed in ACF is smaller compared to the stoichiometric or greater amount required in IF and (ii) the flotation is achieved in a few seconds in ACF whereas gas has to be bubbled for a longer duration in IF.

Kim and Zeitlin[1] have separated Mo by ACF with ferric hydroxide as collector and sodium lauryl sulphate (SLS) as surfactant and estimated Mo by spectrophotometry. Recently Hidalgo *et al.*[2] have preconcentrated Mo in sea water by flotation with iron(III) hydroxide and hexadecyl trimethyl ammonium bromide. They estimated Mo in the floated layer (after removing iron by ion exchange) by differential pulse polarography employing the catalytic wave in nitrate medium. In all the ACF separations of Mo reported so far, iron(III) hydroxide has been used as the collector.[1,2] Iron interferes with the polarographic estimation of Mo when the Fe:Mo ratio is greater than 100. Hence iron has to be separated by ion-exchange or any other suitable method. This additional separation step

can be avoided if iron(III) hydroxide is replaced by aluminium(III) hydroxide. But previous efforts to use aluminium(III) hydroxide as collector were not successful.[2] The present study is aimed at finding out a method of preconcentrating Mo by ACF with aluminium(III) hydroxide as collector.

EXPERIMENTAL

Apparatus

Polarographic measurements were made with a model CL-90 Pulse Polarograph of Elico (P) Ltd., Hyderabad. A Metrohm polarographic cell with mercury pool as counter electrode and SCE as reference electrode was used with a Sargeant capillary having a 3-sec natural drop-time as DME. The rate of flow of mercury was found to be 2.30 mg/sec. For DPP measurements, the pulse duration was 0.04 sec and the pulse amplitude was 50 mV. The droptime was mechanically controlled.

The flotation apparatus was similar to that described by Nakashima.[6] The flotation cell was a tall glass cylinder with a 500-ml capacity fitted with a G-4 porosity sintered glass disc to generate small gas bubbles. A side arm was provided near the bottom of the cell to drain the mother liquor rapidly after flotation.

Purified nitrogen (free from oxygen) was used for deaeration of the solution prior to polarographic measurements as well as for bubbling through the flotation cell.

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Hitachi UV-Visible spectrophotometer (model 139) was used for spectrophotometric determination of some of the added ions present in the froth.

Reagents

All reagents used were of analytical grade. A Mo(VI) (1 mg Mo/ml) stock solution was prepared from ammonium molybdate, Al(III) (10 mg Al/ml) solution from aluminium nitrate and Fe(III) (2 mg Fe/ml) solution by dissolving pure iron powder in diluted hydrochloric acid. Standard solutions of other metals were prepared either by dissolving the pure metal in nitric acid or by dissolving the nitrate salt in water. Eighty per cent (v/v) ethanolic solutions of sodium lauryl sulphate (SLS) (1 mg/ml), sodium oleate (SO) (4 mg/ml) and cetyl trimethyl ammonium bromide (CTAB) (1 mg/ml) were employed. Sodium chloride, sodium nitrate and sodium sulphate were used to study the effect of ionic strength. For the study of anionic interferences, standard solutions of Na_2CO_3, sodium carbonate, sodium hydrogen carbonate and sodium phosphate were used. A standard silicate solution is prepared by dissolving pure silica in sodium hydroxide solution and diluting to volume.

Procedures

Flotation step. Place 400 ml of water containing trace amounts of Mo(VI) in a beaker and add 2 ml of Al(III) solution. Adjust the pH to 5.3 ± 0.1 with aqueous ammonia solution while stirring with a magnetic stirrer. Continue stirring for 10 min. Add 2 ml of SLS solution to the beaker and then transfer the contents to the flotation cell, quantatively. Pass nitrogen at a moderate rate for 1 min. Allow the froth to settle for 2 min. Drain most of the mother liquor through the side arm. The remaining mother liquor is sucked off through the sintered disc. Dissolve the froth in the cell with 10 ml of $2M$ nitric acid and collect is quantitatively in a beaker. Heat this solution to boiling and simmer until the volume is reduced to 1 ml. Make up to 10 ml with water. For the separation of Mo from natural water samples, the above procedure is modified by increasing the solution volume to 1000 ml and Al^{3+} and SLS concentrations to 100 mg and 5 mg respectively.

Polarographic measurement. Transfer a suitable aliquot of the preconcentrated Mo(VI) solution to a polarographic cell. Add 10 ml of a solution containing $2M$ sodium nitrate and $0.5M$ sulphuric acid and dilute to 20 ml so that the solution is $1M$ in sodium nitrate and $0.25M$ in sulphuric acid. After deaeration, record the polarogram from 0.0 to -0.40 V *vs*. SCE at $25°$. Determine the concentration of Mo(VI) by making standard additions of comparable amounts of Mo(VI).

RESULTS AND DISCUSSION

Effect of pH on the flotation behaviour of collectors with surfactants

The flotation behaviour of iron(III) hydroxide and aluminium(III) hydroxide with SLS, SO and CTAB was studied. This was done by adjusting the pH of solutions containing Al(III) and Fe(III) by means of dilute ammonia and nitric acid and floating with an ethanolic solution of surfactant. After flotation, a visual evaluation of the completeness of flotation was made by observing the residual solution and the froth. A clear residual solution, which is free from the collector as shown by quantitative testing, and a stable froth indicate complete flotation. If the flotation is incomplete, the precipitate remains dispersed in the solution. It was found that SLS was able to float ferric hydroxide completely in the pH range 4.5–8.0. Aluminium(III) hydroxide was completely floated in the pH range 5.0–7.5. The flotation was incomplete above pH 7.5 for aluminium(III) hydroxide and above pH 8.0 for iron(III) hydroxide. This was expected, because the isoelectric points (IEP) of the hydroxides of Al(III) and Fe(III) are 7.5 and 8.0, respectively.[15] Flotation of these colloids with other surfactants like SO and CTAB was also dependent on pH. SO floats both aluminium(III) and iron(III) hydroxides completely above pH 7. CTAB floats iron(III) hydroxide partially at low pH values and completely at pH 9–10. With aluminium(III) hydroxide and CTAB, no flotation occurs in the pH range 4–10 and the precipitate remains dispersed in solution.

The results obtained for ferric hydroxide are in agreement with the results of Grieves and Bhattacharya.[16] Matsuzaki and Zeitlin[9] had studied the effect of pH on the ability of various surfactants to float the collectors from aritificial sea water. Their results showed that ferric hydroxide could easily be floated with a number of surfactants while the flotation efficiency was

poor for aluminium hydroxide. The negative results for aluminium hydroxide were probably due to the effect of high ionic strength as found in sea water. No work has been reported on the flotation behaviour of collectors with surfactants from fresh water or water with low ionic strength. We have found that aluminium(III) hydroxide can be completely floated from fresh water samples by SLS in the pH range of 5–7.5 and by SO in the pH range 7–10. When the ionic strength is increased, complete flotation can be achieved by increasing the amount of surfactant to some extent. Above a particular limit, flotation remains incomplete. Further experiments on the flotation of Mo(VI) with aluminium(III) and iron(III) hydroxides were carried out with SLS as surfactant.

Effect of pH on the recovery of Mo(VI) by ACF

Figure 1 shows the effect of pH on the recovery of Mo(VI) using aluminium and ferric hydroxides as collectors and SLS as surfactant. A 100% recovery of Mo(VI) is achieved with aluminium(III) hydroxide in the pH range 5.2–5.5. As the pH is increased, the recovery of Mo(VI) decreases even though the flotation is complete. At higher pH values, the colloid becomes negatively charged and the recovery of molybdate decreases to zero. With iron(III) hydroxide as collector, 100% recovery is obtained in the pH range 4.5–6.0.

In ACF, the mechanism of collection of the analyte on the colloidal precipitate is either adsorption or coprecipitation. In the case of Mo(VI), the pH range for maximum recovery is quite narrow and in this pH range, the colloidal precipitate has a charge opposite to that of the analyte. Hence, it appears that the mechanism governing the separation of Mo(VI) from solution is adsorption. Since Mo(VI) is present as an anion at pH > 1.0, adsorption of this species can be expected to occur at a positively charged colloid. Fe(III) hydroxide and Al(III) hydroxide have positive charges at pH values lower than their IEP's. Above the IEP, there is no electrostatic attraction as both molybdate and the colloidal precipitates are negatively charged. Therefore the adsorption of Mo(VI) decreases almost to zero as the pH is increased to a value above the IEP of the colloidal precipitates (Fig. 1).

Kim and Zeitlin[17] found that Mo(VI) could be completely coprecipitated with colloidal ferric and thorium hydroxides but the recovery of Mo(VI) by coprecipitation on aluminium(III) hydroxide was very poor. They attributed this to the relatively higher solubility of aluminium molybdate compared to ferric and thorium molybdates. The Paneth–Fajans–Hahn rule for the coprecipitation mechanism requires that the collector must contain an ion which forms a compound of low solubility with the counter ion adsorbed. In the light of the above discussion, it may be concluded that the nearly complete recovery of molybdate on aluminium(III) hydroxide by flotation at pH 5.2–5.5 should be due to adsorption.

Effect of ionic strength

The effect of nitrate, chloride and sulphate ions on the recovery of Mo(VI) by ACF with aluminium(III) hydroxide as collector was investigated. The concentrations used for this study were 0.1 ppm Mo(VI), 50 ppm aluminium(III) and 5 ppm SLS. The inert ion concentrations were varied from 0.01 to 0.20M. The pH was adjusted to 5.3 ± 0.1 in all these experiments (Fig. 2). It was found that the doubly charged sulphate ions decreased the percentage recovery of Mo(VI) to a greater extent than singly charged nitrate or chloride ions. When the ionic strength was increased, the recovery of Mo(VI) decreased and the flotation was incomplete at concentrations higher than 0.1M for chloride and nitrate and 0.03M for sulphate. The flotation efficiency was very poor above 0.06M sulphate and 0.2M nitrate or chloride. In the presence of 0.1M chloride or nitrate, 64% of molybdate was recovered by flotation as seen from Fig. 2. The precipitate
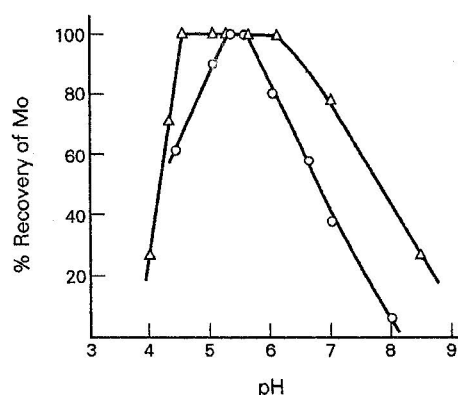

Fig. 1. Effect of pH on the recovery of Mo(IV) with SLS as surfactant and aluminium(III) hydroxide (○) and iron(III) hydroxide (△) as collectors. [Mo(IV)] = 0.20 ppm; [Al(III)] = 50 ppm; [Fe(III)] = 50 ppm; [SLS] = 5 ppm; solution volume = 200 ml.
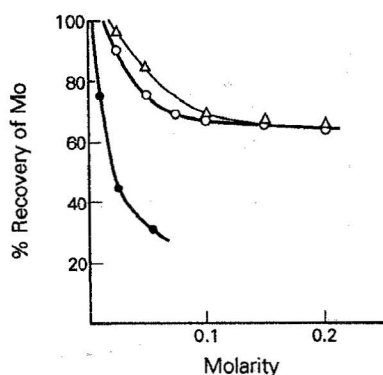
Fig. 2. Effect of ionic strength on the recovery of Mo(VI) with SLS as surfactant and aluminium(III) hydroxide as collector; ($\triangle$) NaNO$_3$, ($\bigcirc$) NaCl and ($\bullet$) Na$_2$SO$_4$. [Mo(VI)] = 0.20 ppm; [Al(III)] = 50 ppm; [SLS] = 5 ppm; pH = 5.3 $\pm$ 0.1.

of aluminium(III) hydroxide remaining in the residual solution after flotation was separated by filtration and Mo(VI) in this residue was estimated. It was found that about 30% molybdate could be recovered from this precipitate showing that Mo(VI) is adsorbed by aluminium(III) hydroxide in the presence of 0.1M chloride or nitrate but the flotation of the collector by the surfactant is affected. The presence of sulphate seriously affected both the adsorption of Mo(VI) and the flotation of aluminium(III) hydroxide.

Effect of the concentrations of surfactant and collector

The effect of SLS on the ACF of Mo(VI) with Al(III) and Fe(III) hydroxides was studied by varying the SLS concentration from 0.2–10 mg. Concentrations of 0.1 ppm Mo(VI) and 50 ppm Al(III) or Fe(III) were used. The pH was maintained at 5.3 $\pm$ 0.1. It was found that 1 mg of SLS was sufficient to float precipitates containing up to 40 mg of Fe(III) or Al(III) in a solution volume of 400 ml (when the ionic strength was less than 0.02M). Recovery of Mo(VI) was maximum when the SLS concentration was in the range 1–4 mg. Higher amounts of surfactant result in the formation of an excess of foam which is not beneficial. If the surfactant concentration exceeds the critical micelle concentration (cmc), the flotation tends to become incomplete. At very low concentrations of surfactant, the foam layer was thin and unstable and could not support the precipitate. Hence a surfactant concentration of 2 mg for a solution volume of 400 ml was used in this work.

The concentrations of Al(III) and Fe(III) were varied from 2–100 mg in a solution volume of 400 ml. SLS concentration was 5 ppm and the pH was adjusted to 5.3 $\pm$ 0.1. When the Mo(VI) concentration was 1–40 μg, an optimum concentration of 10–20 mg Al(III) or Fe(III) was enough to bring about complete recovery of Mo(VI).

Effect of stirring time

The relation between stirring time and recovery of Mo(VI) was investigated. The concentrations of Mo(VI), Al(III) and SLS used were 0.2, 50 and 5 ppm, respectively. The pH was maintained at 5.3 $\pm$ 0.1. It was found that at very low concentrations of colligend (less than 50 μg of Mo), the adsorption of Mo(VI) on the colloidal precipitate was rapid whereas at higher concentrations of Mo(VI), stirring time had an effect on the recovery of Mo(VI). The results obtained are shown in Fig. 3. It is seen that a stirring time of 15 min was needed to get 100% recovery for floating 500 μg of Mo(VI) with 10 mg of aluminium(III) hydroxide. Mo(VI) concentrations of 4, 10 and 40 μg could be collected almost instantaneously. This can be readily explained in terms of the adsorption since it is well known that the rate of adsorption increases when the ratio of adsorbent to adsorbate is large.

The other parameters like gas flow-rate, duration of gas flow and volume of solution had little effect on the recovery of Mo(VI). Gas was bubbled at a moderate rate for 1 min. The solution volume was changed from 100 to 1000 ml. A quantitative recovery of Mo(VI) was obtained.
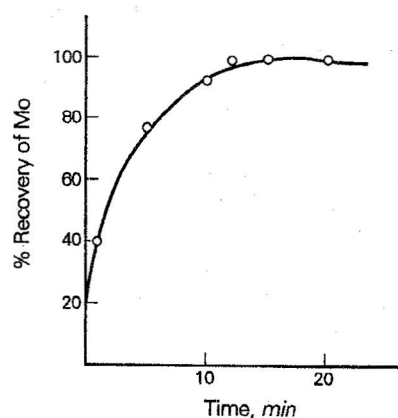

Fig. 3. Effect of stirring time on the recovery of Mo(VI) with SLS as surfactant and aluminium(III) hydroxide as collector; [Mo(VI)] = 500 μg; [Al(III)] = 10 mg; [SLS] = 1 mg; solution volume = 200 ml.

Catalytic wave of Mo(VI) in the presence of surfactants

Following Kannan and Rajagopalan,[18] a supporting electrolyte of $1M$ sodium nitrate and $0.25M$ sulphuric acid was chosen for the catalytic wave polarographic determination of Mo(VI). The catalytic current is sensitive to temperature and hence all the polarograms were recorded at 25°. Hidalgo et al.[2] studied the effect of various surfactants on the catalytic wave of Mo(VI) and found that many of them suppress the peak current. Their report did not include the effect of SLS. In this work, the effect of 5–50 ppm surfactant on the catalytic current (both dcp and DPP) of 1 ppm Mo(VI) was investigated (Fig. 4). It was found that in the presence of 30 ppm SLS, the catalytic current of Mo(VI) was suppressed to about half its original value. But at SLS concentrations less than 10 ppm, the reduction of catalytic current was <20%. However, it was noticed that the catalytic current was virtually unaffected after treatment of the froth with nitric acid. This might be due to the oxidative degradation of SLS into products that are not surface active. The catalytic current of Mo(VI) is affected to a lesser extent by the addition of SO and CTAB as seen from Fig. 4.

Comparison of DPP and CCCDCP for the determination of Mo(VI)

In order to arrive at the best technique from the point of view of improved sensitivity for the estimation of Mo(VI) by the catalytic wave, CCCDCP and DPP were compared both experimentally and theoretically. Typical polarograms (both CCCDCP and DPP) are shown in Fig. 5. Our experiments show that the dc catalytic current is 2.75 times more sensitive than the DPP catalytic current for a droptime of 0.5 sec. When the droptime is increased to 2.0 sec, the ratio of i(CCCDCP) to i(DPP) is increased to 3.4. The pulse duration was 0.04 sec in all the experiments. The ratio of dc catalytic current to DPP catalytic current was calculated with the expression derived by Rodriguez-Monge et al.[19] for EC processes and the values were 2.77 and 3.76 for droptimes of 0.5 and 2.0 sec respectively. Thus it can be seen that the experimental values are in good agreement with the theoretical values. Therefore it may be concluded that the catalytic reduction of Mo(VI) by nitrate is more sensitive by CCCDCP than by DPP. This conclusion contradicts that stated

by Lanza et al.[20] They found DPP to be 4.7 times more sensitive than DCP. This result is difficult to understand since it is contrary to theoretical expectations.

Effects of diverse cations and anions on the flotation and determination of Mo(VI)

The flotation of Mo(VI) was carried out in the presence of various cations and anions. This was done by adding known amounts of these ions to a synthetic solution before flotation.
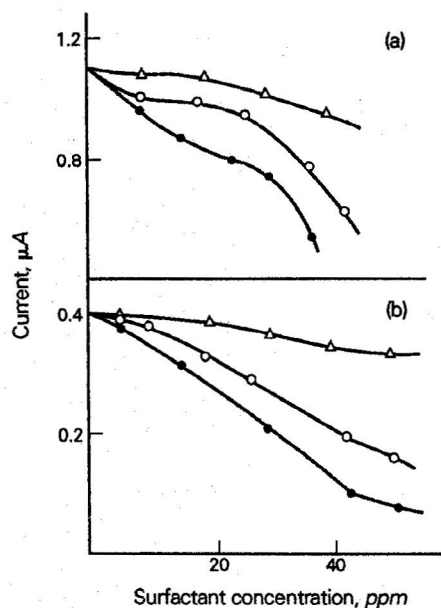
Fig. 4. Effect of variation of surfactant concentration on the catalytic current of Mo(VI); [Mo] = 1 ppm, time = 0.5 sec (a) dc catalytic current (b) DPP catalytic current; (△) SO, (○) CTAB and (●) SLS.
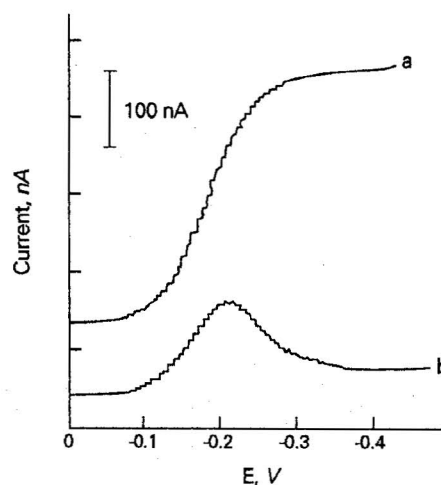
Fig. 5. Typical polarograms of Mo(VI) in a supporting electrolyte of $1M$ NaNO$_3$ and $0.25M$ H$_2$SO$_4$. [Mo] = 0.1 ppm; $m = 2.30$ mg/sec; time = 2 sec (a) CCCDCP and (b) DPP, $\triangle E = 50$ mV.

The results are summarized in Tables 1 and 2. The amounts of added ions in the froth after flotation at pH 5.3 ± 0.1 were determined either by polarography or by spectrophotometry. Cu(II), Pb(II), Ni(II), Co(II), Bi(III), Sb(III), Zn(II) and Cd(II) in the froth were estimated by polarography. Fe(III), Ti(IV), Zr(IV) and Cr(III) in the froth after flotation were determined by conventional spectrophotometric methods. Fe(III), Bi(III), Ti(IV), Cr(III) and Zr(IV) were floated completely along with Mo(VI). These elements with the exception of Fe(III) do not interfere with the polarographic determination of Mo. The recoveries of Cu(II) and Pb(II) were 75–80%. Co(II), Ni(II), Zn(II), Cd(II) and Sb(II) were partially floated.

Table 2 gives the results obtained on studying the effect of anions on the flotation of Mo. The flotation efficiency of Mo was affected by the presence of phosphate and silicate. Thus the recovery of Mo is reduced to 56 and 61% by 50 ppm levels of silicate and phosphate respectively. The interference was found to be negligible at or below 5 ppm silicate and phosphate. At higher concentrations, these multivalent anions compete with molybdate in the process of adsorption on the collector and thus cause a lower recovery for Mo(VI). Anions like carbonate and bicarbonate could be tolerated to a level of 1000 ppm in the solution.

The effect of various cations and anions on the catalytic wave of Mo(VI) was investigated.

Table 2. Effect of the presence of anions on the flotation of Mo. [Mo(VI)] = 40 μg; [Al(III)] = 20 mg; [SLS] = 1 mg; pH = 5.3 ± 0.1; solution volume = 200 ml

Ion	Amount of ion added, mg	Mo recovery, μg	Recovery, %
SiO_3^{2-}	1.0	38.0	95.0
	2.0	35.0	87.5
	4.0	32.8	82.0
	10.0	22.4	56.0
PO_4^{3-}	1.0	38.4	96.0
	2.0	36.0	90.0
	4.0	35.0	87.5
	10.0	24.4	61.0
CO_3^{2-}	10.0	39.2	98.0
	50.0	39.1	97.8
	100.0	38.0	95.0
	200.0	38.4	96.0
HCO_3^-	100.0	39.0	97.5
	200.0	38.0	95.0

The concentration of Mo(VI) in the supporting electrolyte was 0.2 ppm. The results are given in Table 3. The catalytic current of Mo(VI) is not affected by the presence of a 100-fold excess of silicate and phosphate. A 100-fold excess of metallic ions such as Pb(II), Cd(II), Zn(II), Ni(II) and Co(II) do not interfere as their reduction potentials are more negative than that of Mo(VI). A 1000-fold excess of Al(III) and 100-fold excess of Ti(IV) and Zr(IV) also do not interfere. Cu(II) and Bi(III) peaks occur at a more positive potential than that of Mo(VI). But since the peaks are separated by more than 150 mV and the sensitivities of copper and bismuth are much less than that of Mo(VI)

Table 1. Effect of the addition of other metallic ions on the flotation of Mo with Al(OH)₃ as collector and SLS as surfactant. [Mo(VI)] = 40 μg; [Al(III)] = 20 mg; [SLS] = 1 mg; pH = 5.3 ± 0.1; solution volume = 200 ml

Ion	Ratio of Mo(VI) to the added ion	% Recovery Mo(VI)	% Recovery Added ion
Pb(II)	1:1	100	80
	1:10	>95	75
	1:25	>95	75
Cu(II)	1:1	100	75
	1:10	>95	75
	1:25	>95	75
Fe(III)	1:1	100	100
	1:100	95	>95
Bi(III)	1:1	100	>95
	1:25	96	>95
Ti(IV)	1:10	100	100
	1:100	>95	>95
Zr(IV)	1:100	>95	>95
Cr(III)	1:1	100	>95
	1:10	>95	>95
Cr(IV)	1:1	>95	—
Co(II)	1:1	>95	7
Ni(II)	1:1	>95	12
Cd(II)	1:10	>95	5
Zn(II)	1:10	>95	50

Table 3. Interferences due to foreign species in the polarographic determination of Mo. [Mo(VI)] = 0.2 ppm; time = 0.5 sec; ΔE = 50 mV

Ion	Concentration ratio, ion: Mo(VI)	Error %
Pb(II), Cd(II), Zn(II), Co(II), Ni(II), Cr(III), Ti(IV), Zr(IV)	100:1	nil
Al(III)	1000:1	nil
Cu(II), Bi(III)	25:1	nil
Sn(IV)	10:1	nil
	50:1	−13
Fe(III)	40:1	nil
	100:1	−10
	200:1	−25
	400:1	−55
Cr(VI)	10:1	−6
Tl(I)	10:1	−6
Sb(III)	1:1	+13
	2:1	+25
Sb(V)	10:1	nil
SiO_3^{2-}	100:1	nil
PO_4^{3-}	100:1	nil

in nitrate medium, it is possible to determine Mo(VI) in the presence of a 25-fold excess of Cu(II) and Bi(III). In such cases, DPP offers better resolution than CCCDCP. Hence in the presence of an excess of Cu(II) and Bi(III), it is preferable to use DPP for the determination of Mo. A 10-fold excess of Cr(III), Cr(VI), Tl(I) and Sn(IV) does not interfere. Fe(III) does not interfere if present in small amounts but a 100-fold excess of Fe(III) causes a decrease in the Mo catalytic current by 10%. When the Fe:Mo ratio is 400, there is a significant reduction in the catalytic current of Mo(VI) as seen from Table 3. Sb(III) interferes as its reduction peak coincides with that of Mo(VI). It is seen that Sb(III) gets partially floated with Mo(VI). The interference was overcome by oxidizing Sb(III) to the electroinactive Sb(V) by adding a few drops of potassium permanganate solution to the solution of froth.

Recovery of Mo(VI) from synthetic solutions

Initial experiments were carried out with 1 ppm Mo(VI), 10 mg Al(III) and 1 mg SLS in a solution volume of 400 ml to standardize the experimental conditions. Then under the standardized conditions, the flotation was done at lower Mo(VI) concentrations and the results are given in Table 4. Thus it was seen that 1 μg of Mo in 400 ml of water could be preconcentrated by this method.

The detection limit (at a signal-to-noise ratio of 3) is 5.0 μg/l. for CCCDCP and DPP at a droptime of 2 sec. When the initial volume of water for flotation was increased to 1000 ml, the concentration factor was 50. Thus it was possible to achieve a detection limit of 0.1 μg/l. for Mo(VI) in water by this flotation-polarographic method. This value is comparable to the detection limit obtained by adsorption voltammetry.[21] The relative standard deviation for 8 replicate analyses of a solution containing 2 μg/l. Mo was found to be 3.0%.

Recovery of Mo from natural fresh water samples

It was noticed that the recovery of Mo from natural fresh water by ACF under the experimental conditions standardized for synthetic solutions [50 ppm Al(III), 5 ppm SLS and pH 5.3 $\pm$ 0.1] was about 50%. Fresh water samples often contain anions like carbonate, bicarbonate, chloride, silicate and phosphate in addition to some metal ions. The approximate ranges and typical values for some metals and ligands in fresh waters have been reported elsewhere.[22]

Table 4. Results for the analysis of synthetic water samples*

No.	Mo(IV) added, μg	Mo(IV) found, μg	Recovery %
1	1.0	1.0	100
2	1.6	1.56	97.5
3	8.0	7.84	98.0
4	40.0	39.0	97.5
5	500.0	495.0	99.0

*Solution volume = 400 ml.

The results of the study of anionic interference on the flotation of Mo(VI) are already given in Table 2. The concentrations of Mo(VI), Al(III) and SLS used for this study were 0.2 ppm, 100 ppm and 5 ppm. It can be seen from Table 2 that up to 1000 ppm of carbonate and bicarbonate do not interfere with the flotation of Mo whereas the recovery of Mo is affected by silicate and phosphate at concentrations higher than 10 ppm. But the typical concentrations of phosphate and silicate in fresh water are of the order of 1 and 5 ppm respectively. We found that the recovery of Mo from natural water samples could be improved by increasing the collector concentration to 100 ppm. The alternative method is to repeat the flotation until all the Mo was recovered. The recovery of Mo was about 90% in a single flotation by employing 100 ppm Al(III). Two consecutive flotations with 50 ppm Al(III) also enabled us to recover 90% Mo but a single flotation with increased amount of collector and surfactant was less time consuming than double flotations.

Iron and copper present in natural water were also floated along with molybdenum. Copper does not interfere in the determination of Mo. The iron to molybdenum ratio was often higher than 100 in the froth and this decreased the sensitivity of molybdenum determination by catalytic wave polarography. By examining water samples from different sources like wells, lakes and borewells, we found that the Fe(III) to Mo(VI) ratio in the froth often exceeded 500. This suppresses the polarographic signal considerably and results in lower values for Mo. Hence it is essential to remove iron which is done by incorporating an additional flotation step prior to the flotation for the preconcentration of Mo.

Since the recovery of Mo(VI) falls to zero at pH values above 8.0, it is possible to separate Fe(III) from Mo(VI) by employing a flotation step. Therefore, for the determination of Mo in natural water samples containing considerable amounts of Fe(III), the procedure is modified

Table 5. Results for the determination of Mo(VI) in fresh water samples

No.	Sample*	Mo(VI) found† ($\mu g/l$)
1	A	0.42 ± 0.04
2	B	0.50 ± 0.04
3	C	0.64 ± 0.05
4	D	0.31 ± 0.03

*A = laboratory tap water; B = well water; C = bore-well water; D = lake water.
†Mean ± standard deviation ($n = 4$).

as follows: add 20 mg of Al(III) to 1000 ml of the sample solution, adjust the pH to 8.5 with dilute ammonia, add an ethanolic solution containing 5 mg of sodium oleate and float by bubbling nitrogen through the solution for 2 min. Fe(III) and other cations like Cu(II) and Pb(II) if present are separated in the froth. To the residual solution, add 100 mg of Al(III), adjust the pH to 5.3 ± 0.1, add 5 mg of SLS and continue as described earlier in the experimental section. Mo(VI) in four natural water samples from different sources was estimated with this procedure and the results obtained are shown in Table 5. The reproducibility was good. Thus the method is found to have great potential in determining nanogram levels of Mo(VI) in natural fresh water samples.

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