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Spectrophotometric determination of molybdenum in steel samples utilizing selective sorbent extraction on Amberlite XAD-8 resin

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Abstract

A preconcentration procedure, using a short column filled with Amberlite XAD-8, is proposed for the spectrophotometric determination of traces of molybdenum. Molybdenum as a Mo(V)– thyiocyanate complex is sorbed strongly on the resin and is easily eluted with acetone. The molybdenum complex in the effluent can be determined spectrophotometrically at 462.0 nm. The influence of several ions, as interferents, was discussed. The procedure was applied to the determination of molybdenum in steel with satisfactory results (recovery $\geq 95\%$; relative error $\leq 3\%$; relative standard deviation $\leq 5\%$ in the concentration range of 0.006–0.024%; IUPAC detection limit, 60 μg l^{-1} in solution).

Keywords: Molybdenum; Steel; Spectrophotometry; XAD-8 resin

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1. Introduction

Many methods have been proposed for the spectrophotometric determination of molybdenum [1–4]. The most commonly used are based on measuring the absorbance of the molybdenum(V)–thiocyanate complex after liquid–liquid extraction. It has been adopted to solid state extraction using an ion exchanger resin or polyurethane foam [5,6]. The liquid– liquid extraction procedure, however has not been adopted to XAD sorbent extraction, but, we have reported that the Mo(V)–SCN complex was retained qualitatively by a column filled with Amberlite XAD resin [7]. This induced us to study the quantitative preconcentration of molybdenum as a Mo(V)–SCN complex on a column filled an XAD resin.

This paper describes the systematic investigation of column separation and preconcentration of molybdenum as a thiocyanate complex from acidic solutions, on Amberlite XAD-8 resin, a polyacrylic acid ester, in a column. Molybdenum retained was eluted with acetone. The analyte in the effluent was determined spectrophotometrically. The method was used for the determination of Mo in steel samples.

2. Experimental

2.1. Apparatus

A Hitachi 150-20 spectrophotometer with a 10 mm quartz cell was used for absorbance measure-

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ments. The determination of molybdenum as the Mo(V)–SCN complex was performed at 462.0 nm.

2.2. Reagents and solutions

All chemicals, purchased from commercial sources, were of analytical grade. Doubly distilled–deionised water was used for the preparation of all the solutions.

An approximately 1000 μg ml^{-1} stock solution of molybdenum was prepared by dissolving an appropriate amount of sodium molybdate dihydrate in water containing 1 ml of conc. HCl and diluting it to 1000 ml. The stock solution was standardized gravimetrically by the 8-quinolinol method [8]. Appropriate standard and test solutions of Mo were prepared daily from this solution by dilution with water. Tin(II) chloride solution, 40% (w/v), was prepared in 1 M hydrochloric acid. Ammonium thiocyanate, 25% (w/v), was prepared in water. To prepare iron(III) chloride solution, 1% (w/v) in water, $FeCl_3 \cdot 9H_2O$ was used. The solution of 1% (w/v) citric acid was prepared in water.

Amberlite XAD-8 resin (Merck, Darmstadt) was treated as described previously [9,10].

2.3. Column preparation

A glass column, 10 × 100 mm, having a fritted glass disc over its stopcock, was used. The resin column was prepared by aspirating a water slurry of Amberlite XAD-8 (500 mg) into the column.It was conditioned with 10–15 ml of the blank solution used for the experiments in this study.

2.4. Procedures

2.4.1. Preconcentration of Mo with Amberlite XAD-8

An aliquot of stock solution containing 2–20 μg Mo(VI) was transferred into a beaker and 50 μl of 1% Fe(III) solution, 750 μl of 25% NH_4SCN solution 1500 μl of 40% $SnCl_2$ solution and 1 ml of 10 M H_2SO_4 were added. The solution was diluted to 50–100 ml with water and left at room temperature for 10–15 min to allow complete formation of the Mo(V)–SCN complex. This solution was drawn through the column at flow rates of about 10–15 ml min^{-1} using a reduced pressure. After complete passage of the solution, the column was washed with the blank solution (100 ml), and the Mo(V)–SCN complex retained was eluted with 2–10 ml of acetone at a flow rate of 1–2 ml min^{-1}. The effluent was used directly for the spectrophotometric determination of molybdenum as the thiocyanate complex at 462.0 nm.

2.4.2. Determination of Mo in steel samples

0.1–0.3 g amounts of steel samples were accurately weighed into a 100 ml beaker and treated with 10–15 ml of conc. HCl. The beaker was covered and heated gently to dissolve the sample. Then, 5–10 ml of conc. HNO_3 was added, the heating was continued and the solution was evaporated to near dryness to expel oxides of nitrogen. The residue was dissolved in 3 ml of conc. HCl and 20 ml of water. The solution was heated for 10 min and then cooled. The final volume was made up to 50–100 ml with water. The molybdenum content of this solution was determined by following the sorption procedure described above, first adding 2 ml of 1% (m/v) citric acid solution as a masking agent.

3. Results and discussion

3.1. Influence of experimental variables

Mo(V), formed by reduction of Mo(VI) with $SnCl_2$ in sulfuric acid solution, forms an orange–red Mo(V)–thiocyanate complex. The effect of amounts of reagent on the sorption of the complex on a column of XAD-8 resin and on the spectrophotometric determination of the Mo(V)–thiocyanate complex was investigated. As seen in Fig. 1, Mo was retained quantitatively ($\geq$ 97%) from a solution including 50 μl of 1% $FeCl_3$, and 0.5–3 ml of 10 M H_2SO_4, 0.5–5 ml of 25% NH_4SCN 0.5–5 ml of 40% $SnCl_2$. The addition of Fe(III) at a minimum amount to the sample solution is suggested to enhance the sensitivity and stability of the Mo(V)–SCN complex [11]. The effect of Fe(III) concentration required was also tested for the recovery of Mo. The volume of 1% $FeCl_3$ solution from 25 μl to 500 μl has no effect on the recovery, but a large excess has a positive interference. It is well-known that the Fe(III)–SCN complex is retained by a column of XAD-8 [12]. In

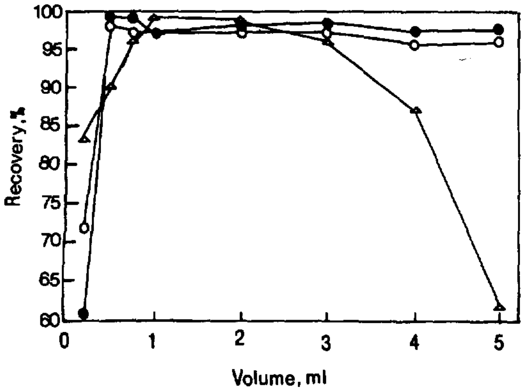

Fig. 1. Influence of reagent amounts on recovery of molybdenum with 10 M H_2SO_4 (△), 25% NH_4SCN (○) and 40% $SnCl_2$ (●). The solutions, prepared with the indicated amount of examined reagent, contained the other two reagents at their optimum amounts, see text.

addition, the position of the absorption maximum for the complex varies between 470 and 530 nm, depending on the medium [3]. The interference is probably due to these phenomena. However, the effect can be prevented by the reduction of Fe(III) to Fe(II) with an excess of $SnCl_2$, the amount of excess $SnCl_2$ depending on the concentration of iron(III) in the sample solution.

As a result of this investigation, 1 ml of 10 M H_2SO_4, 50 μl of 1% $FeCl_3$, 1 ml of 25% NH_4SCN and 1.5 ml of 40% $SnCl_2$ solutions as optimum amounts were added to the sample solution for further study.

Mo as a thiocyanate complex has been determined in aqueous solution and various organic solvents like alcohols, ethers and some ketones. Acetone is rarely used [3,13]. In this study, the complex is formed in aqueous solution, retained by the column, and extracted from the column by acetone for spectrophotometric determination. For this reason, the accuracy and precision of the results was strongly depended on the standing time allowed for the formation of the complex. The maximum absorbance of the complex in aqueous solution was attained within 10–15 min and thereafter gave constant absorbance readings for at least 5 h. Also, the absorbance of the complex eluted into acetone remained unchanged for 5 h. However, the determination of Mo by the recommended procedure may be completed within 30 min.

To obtain a high concentration factor, 10 μg of molybdenum in test solutions prepared under optimized conditions was concentrated from 100–1000 ml of sample. Mo could be recovered quantitatively from up to 500 ml of sample solution. The volume of acetone as eluent is also important for achieving a high concentration factor. This was examined by varying the acetone volume up to 10 ml. The smallest volume of acetone found to give quantitative elution was 2 ml. In this case, the highest concentration factor was calculated to be 250.

The preconcentration capacity of a column filled with 500 mg XAD-8 resin was determined with increasing amounts of Mo from 2 to 1000 μg in 100 ml of solution. The recoveries of Mo were found to be $\geq 95\%$ for 2–100 μg, ca. 85% for 100–500 μg and $\leq 70\%$ for > 500 μg Mo.

3.2. *Effect of diverse ions on recovery*

In order to assess the possible analytical applications of the recommended procedure, the effect of some foreign ions which interfere with the determination of molybdenum by the thiocyanate–tin(II) chloride method often accompany Mo in various real samples, such as natural waters, soils and steels, was examined. For this study, a fixed amount of Mo (10 μg) was taken with different amounts of foreign ions and the recommended procedure was followed. The tolerance limit was defined as the largest amount of foreign ions that produced an error not exceeding ±5% in the determination of Mo by the combination of the column preconcentration and the spectrophotometric determination methods. The results are summarized in Table 1. As can be seen, a large number of ions used have no significant effect on the determination of Mo. The most serious interferences were from W(VI), Cu(II), Co(III) and Fe(III) ions. Interferences from these ions are probably due to the complex formation with thiocyanate ion and sorption of these complexes on XAD-8 resin.

Greater tolerance limits for these ions can be achieved by using several masking methods. In order to eliminate the interferences of W(VI), Cu(II), Co(III) and Fe(III) ions, tartaric acid, citric acid or EDTA can be used as a masking agent [14,15]. Citric acid was selected from these because of its suitability for W(VI), Cu(II) and Co(III) found in some

Table 1
Tolerance to diverse ions on the recovery of 10 μg Mo from Amberlite XAD-8 (sample volume: 100 ml, $n = 4$)

Ion	Added as	Tolerable limits (mg)
Chloride	NaCl	3000
Nitrate	$NaNO^3$	250
Phosphate	$NH_4H_2PO_4$	500
Iodide	NaI	500
Citrate	Citric acid	500
Tartrate	Sodium tartrate	500
Na(I)	NaCl	3000
K(I)	KCl	1000
Mg(II)	$MgCl_2$	1000
Ca(II)	$CaCl_2$	1000
Ba(II)	$Ba(NO_3)_2$	100
Sr(II)	$Sr(NO_3)_2$	100
Al(III)	$Al(NO_3)_3$	75
Mn(II)	$Mn(NO_3)_2$	75
Mn(VII)	$KMnO_4$	50
Ni(II)	$Ni(NO_3)_2$	50
Cd(II)	$Cd(NO_3)_2$	25
Bi(III)	$Bi(NO_3)_3$	25
Cr(VI)	$K_2Cr_2O_7$	25
Cr(VI)	K_2CrO_4	20
Cr(III)	$Cr(NO_3)_3$	20
Zn(II)	$Zn(NO_3)_2$	10
Fe(III)	$FeCl_3$	5
W(VI)	Na_2WO_4	0.030(5) [a]
Cu(II)	$Cu(NO_3)_2$	0.050(10) [a]
Co(III)	$Co(NO_3)_3$	0.100(10) [a]

[a] The limits in parentheses were obtained with 1 ml of 1% citric acid solution added.

preliminary experiments. Interferences from W(VI) up to 5 mg and Cu(II) and Co(III) up to 10 mg were eliminated by addition of 1 ml of 1% citric acid solution. However, the optimum amount of citric acid required to eliminate the interferences from W(VI), Cu(II) and Co(III) is a function of their amounts in the sample solution. The masking agent, above a certain tolerance limit, can also interfere (Table 1), but the limit for citric acid is quite high, so there is no problem with use of the amount of the citric acid recommended for the masking procedure. Unfortunately, citric acid was ineffective in removing the interference of Fe(III), so in order to eliminate the interference of Fe(III) tin(II) chloride reduction was used, as indicated above.

3.3. Analytical performance

Acetone has been found to be the most suitable eluent for columns filled with Amberlite XAD resins [7], and has been used in this study. The use of acetone in both elution and determination steps decreases the period of analysis because evaporation of the effluent was not necessary. In addition, acetone improved the analytical performance of the determination step. For example, while Beer's law was obeyed between 1×10^{-5}–8×10^{-5} M molybdenum when water was used as solvent, it was obeyed

Table 2
Determination of molybdenum in steel samples

Steel sample	Contents of other elements (%)			Molybdenum content (%)	
				Spark-AES	Present method [a]
703496S2	0.064C,	0.004Si,	0.237Mn	0.024	0.0245 ± 0.0005
	0.009P,	0.011S,	0.028Al		
	0.040Cu,	0.071Cr,	0.044Ni		
734606S2	0.374C,	0.268Si,	0.729Mn	0.022	0.0220 ± 0.0004
	0.012P,	0.002S,	0.025Al		
	0.118Cu,	0.160Cr,	0.053Ni		
734603S2	0.315C,	0.238Si,	0.972Mn	0.014	0.0137 ± 0.0005
	0.015P,	0.012S,	0.038Al		
	0.103Cu,	0.056Cr,	0.053Ni		
703498S2	0.073C,	0.009Si,	0.302Mn	0.006	0.0058 ± 0.0002
	0.015P,	0.008S,	0.032Al		
	0.032Cu,	0.041Cr,	0.047Ni		
00106013	0.650C,	0.230Si,	0.732Mn	–	0.0091 ± 0.0005
	0.017P,	0.037S,	0.180Cu		
	0.161Cr,	0.190Ni			

[a] $x \pm ts/\sqrt{n}$, $n = 5$, $P = 0.95$.

between 2×10^{-6}–5×10^{-5} M in acetone. The apparent molar absorptivities were 4791 l mol^{-1} cm^{-1} for water and 20142 l mol^{-1} cm^{-1} for acetone in the analytical range above. The IUPAC detection limit was found to be 60 μg l^{-1} ($k = 3$, $n = 21$) [16] in the final solution.

3.4. Determination of the Mo content in steel samples

A standard reference material for steel samples was not available to the authors. For this reason, the procedure was applied to the determination of Mo in steel samples analyzed by spark atomic emission spectroscopy (spark-AES). For comparison, the results are given in Table 2. The results for the molybdenum content of the samples agreed with the data obtained by spark-AES. The analytical errors in the concentration range 0.006–0.024% were < 3% and relative standard deviations were < 5%.

3.5. Conclusions

The classical spectrophotometric thiocyanate method used for molybdenum determination has been successfully adopted to XAD sorbent extraction.In comparison with liquid–liquid extraction, sorbent extraction leads to a high preconcentration factor by using a large sample volume and a small volume of eluting agent. With the spectrophotometric determination of molybdenum in the effluent, sensitivity is increased and the period of analysis is decreased. Instead of the use of fresh solvent as the extracting phase for each sample, 500 mg of XAD-8 resin can be used repeatedly for at least 300–400 samples.

The procedure has been applied to determine Mo in some steel samples with satisfactory results. Because of insensitivity to interference from the most common matrix elements, including the alkaline and alkaline earth metals, aluminum and iron, etc., the procedure offers attractive possibilities for the preconcentration and determination of molybdenum in various other matrices.

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