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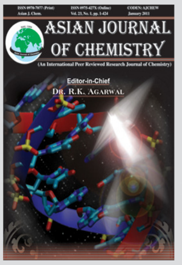

Selective Spectrophotometric Method for the Determination of Molybdenum in X80 Pipeline Steel

SHAO XIAODONG[1,*], LI YING[2], LIU YANGQIN[1] and LI FAGEN[1]

[1]CNPC Tubular Goods Research Institute, No. 32 Dianzier Road, Xi'an 710065, P.R. China
[2]Xi'an Thermal Power Research Institute Co. Ltd., No. 136 Xingqing Road, Xi'an 710032, P.R. China

*Corresponding author: E-mail: shaoxd@163.com

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A highly selective and sensitive spectrophotometric method for the determination of molybdenum in high grade pipeline steel has been presented. This method was based on the chromogenic reaction between molybdenum(V) and sodium thiocyanate. Employing stannous chloride as a reductant, molybdenum(VI) was reduced to molybdenum(V) at the room temperature. The obtained molybdenum(V) formed an orange-red-coloured (1:5) ligand complex with thiocyanate. The absorbance of the complex was measured at 470 nm and the molar extinction coefficient (ε) is 1.75×10^4 L mol^{-1} cm^{-1}. Under the optimum reaction conditions the absorption value was proportional to the concentration of molybdenum in the range of 0.11-0.89 % (w/w) and the relative standard deviation was less than 3.0 %. The proposed method was free from the interference from a large number of analytical important elements and has been applied satisfactorily to the determination of molybdenum in X80 pipeline steel and X70 pipeline steel samples with the improved accuracy and precision.

Key Words: Molybdenum, Spectrophotometry, Chromogenic reaction, X80 pipeline steel.

INTRODUCTION

Pipeline system is the main form of transportation for oil and natural gas. High grade pipeline steel can effectively improve the security of long-distance transportation and to reduce costs, will become the main steel for gas pipeline project[1]. China West-East Natural Gas Transmission Pipeline Project has been completed for the X70 grade pipeline steel, building of the Second West-East Natural Gas Transmission Pipeline Project mainly steel grade is the X80 steel. It was well known that molybdenum is an important element for high grade pipeline steel. Molybdenum is valuable alloying agents and coexists in a number of industrially important alloys and steels. Molybdenum is found in special alloys and steels to increase heat and corrosion resistance in solutions and alkali metal vapours, these materials being refractory and exhibiting high coefficients of elasticity and shear moduli[2]. Owing to their increasing industrial applications of molybdenum, the determination of trace amounts of molybdenum is of great interest. Therefore, it is important from the analytical point of view to develop simple, sensitive and reliable methods for the trace level determination of molybdenum in various complex matrixes.

Various analytical techniques used for the determination of molybdenum in different types of matrices including electroanalytical chemistry method[3], neutron activation analysis[4], inductively coupled plasma atomic emission spectrophotometry[5,6], X-ray fluorescence[7] and spectrophotometry[8-12]. Spectrophotometric methods occupy special position due to their simplicity, less expensive instrumentation and high sensitivity. A number of chromogenic reagents, such as 3-hydroxy-2-(4-methoxyphenyl)-6-propionyl-4-oxo-4*H*-1-benzopyran, isothipendyl hydrochloride, pipazethate hydrochloride, 3,4-dihydroxybenzoic acid, O,O′-*bis*(2-ethylhexyl)dithiophosphoric acid, 2-(2′-furyl)-3-hydroxy chromone, N-hydroxy-N,N′-diphenylbenzamidine[13-16] have been reported for the determination of molybdenum at trace levels. The reagent, resacetophenone *p*-hydroxybenzoylhydrazone[17], though reports higher sensitivity, but the conditions of colour reaction, such as pH and surfactant concentration must be strictly controlled in order to obtain reliable results. Most of the reported methods suffer from a number of limitations, such as lack of sensitivity, require tedious and time consuming extraction, preconcentration using an ion-exchanger resin, reduction to lower oxidation state, followed by colour development and extraction or lack of selectivity. However, this present method is based on the chromogenic reaction between molybdenum(V) and sodium thiocyanate. Employing stannous chloride as a reductant, molybdenum(VI) was reduced to molybdenum(V) at the room temperature. The obtained molybdenum(V) formed an orange-red-coloured (1:5) ligand complex with thiocyanate. The absorbance of the complex was measured at 470 nm and the molar absorptivity was 1.75×10^4 L mol^{-1} cm^{-1}. Under the optimum reaction conditions the absorption value was proportional to the concentration of molybdenum in the range of 0.11-0.89 % (wt/wt) ($R^2 = 0.9999$) and the relative standard deviation (RSD) was less than 3.0 % (n = 5). The proposed method is free from the interference from a large number of analytical important elements and has been applied satisfactorily to the determination of molybdenum in X80 pipeline steel and X70 pipeline steel samples with the improved accuracy and precision.

EXPERIMENTAL

A UV-visible spectrophotometer (Model TU-1901, Beijing Persee General Instrument Co. Ltd.) with 2.0 cm quartz cells was employed for all absorbance measurements.

All chemicals including hydrochloric acid, sulphuric acid, phosphoric acid, perchloric acid and nitric acid (Xi'an Chemical Reagent Plant) used in the experiments were of analytical reagent grade and were used as received. Solutions of sodium thiocyanate and stannous chloride were prepared daily by dissolving the reagents in deionized water treated with a Milli-Q water purification system (Millipore, Bedford, MA, USA). Solutions of molybdenum were prepared from the steel certified reference materials (CRM) including GBW01308, GBW01309, GBW01310, GBW01311, GBW01312 (Institute of Anshan Iron and Steel Group Corporation), GBW01356a (China Iron & Steel Research Institute Group), YSBC15206 (Institute of Taiyuan Iron and Steel Group Corporation). All working strength solutions in the experiment were prepared in deionized water.

General procedures: Weigh accurately 0.2500 g of drilled low alloy steel samples and dissolve the sample in mixture of sulphuric acid and phosphoric acid on a 250 mL taper bottle. Continue the treatment with mixture acid till the sample goes into solution and heat to fumes of oxides of nitrogen, sulphuric acid and evaporate almost to dryness. Cool the solution, add 20 mL deionized water to dissolve some materials. Finally, dilute the solution to 100 mL in a volumetric flask with deionized water. Then, transfer 10 mL of the above stock solution in a 50 mL volumetric flask. Add 4 mL of 50 % (v/v) solution of sulphuric acid, 10 mL of 17 % (v/v) solution of perchloric acid and 10 mL of 100.0 mg mL^{-1} solution of sodium thiocyanate. Add 10 mL of 100.0 mg mL^{-1} stannous chloride solution to reduce molybdenum(VI) to the lower oxidation states, followed make up to the mark with 5 % (v/v) solution of sulphuric acid, mix well and let stand for 15 min. Measure the absorbance at 470 nm using a UV-visible spectrophotometer with 2.0 cm quartz cells against a reagent blank prepared similarly. Plot the amount of molybdenum in the sample solution against absorbance to obtain the calibration graph.

RESULTS AND DISCUSSION

Spectral characteristics: The absorption spectra of the reagents blank, molybdenum-thiocyanate ligand complex against the reagent blank were tested. The molybdenum-thiocyanate ligand complex yields the maximum absorption at 470 nm. However, the absorption spectrum of the reagents blank under similar conditions showed that it does not absorb at 470 nm. And the experimentation also demonstrated that molybdenum increases the absorbance value considerably, resulting in increased sensitivity of the method. Therefore, measure the absorbance of molybdenum-thiocyanate orange-red-coloured ligand complex at 470 nm.

Select dissolved acid for low alloy steel samples: The effect of the different acids for dissolve the low alloy steel samples was examined. It was found that a solution mixed with 15 % (v/v) sulphuric acid and 15 % (v/v) phosphoric acid has a good effect for dissolve the low alloy steel samples. Thus, an acid solution mixed with 15 % (v/v) sulphuric acid and 15 % (v/v) phosphoric acid was recommended for dissolve the low alloy steel samples in subsequent studies.

Influence of the amounts of chromogenic reagent: Sodium thiocyanate was selected as the chromogenic reagent in the proposed method. The effect of the chromogenic reagent was examined by measuring the absorbance of solution containing certain amounts of molybdenum and variable amounts of sodium thiocyanate. It was found that 10 mL of 100.0 mg mL^{-1} sodium thiocyanate solution sufficed to complex the amounts of molybdenum taken; with higher concentrations the absorbance was essentially constant. Ten mL of 100.0 mg mL^{-1} sodium thiocyanate solution were recommended as a suitable amount of chromogenic reagent.

Select reductant and influence of acids: The chromogenic reaction between molybdenum-thiocyanate complex and ascorbic acid in water is slow at room temperature and best results with maximum sensitivity are obtained for 2 h. It has been further observed that the chromogenic reaction of molybdenum-thiocyanate occurs immediately even at room temperature if stannous chloride is used. The effect of acids on the formation of mixed ligand complex has been studied in hydrochloric acid, sulphuric acid, phosphoric acid or nitric acid medium. It was found that the maximum intensity of the orange-red colour is achieved in 50 % (v/v) sulphuric acid and 17 % (v/v) perchloric acid within 15 min. The absorbance values remain constant for 1 h. In the presence of other acids, maximum intensity of the colour cannot be reached indicating the unstable nature of the coloured species in these media. All subsequent studies are carried out in sulphuric acid and perchloric acid medium.

Sequence of addition of reagents: From experiments in which sulphuric acid, perchloric acid, sodium thiocyanate and stannous chloride were added in all possible orders. It was found that there is no appreciable change in the colour of the complex and the variations in the absorbance values. These phenomena demonstrate that the reaction between molybdenum and thiocyanate is independent of the order of addition.

Stoichiometry and stability constant: The stoichiometry of the molybdenum complex with thiocyanate in solution was studied spectrophotometrically by Job's method of continuous variation and equilibrium shift method. The results indicate that the molar ratio of molybdenum to thiocyanate is 1:5. These methods further confirmed the formula of mixed-ligand complex as $[MoO(SCN)_5]^{2-}$.

$$MoO^{3+} + 5SCN^- \rightarrow [MoO(SCN)_5]^{2-}$$

The molar extinction coefficient (ε) of the orange-red-coloured (1:5) ligand complex is 1.75×10^4 L mol^{-1} cm^{-1}, which calculated from these results following the described method.

Preparation of the calibration graph: Under the optimal conditions, a series of standard solutions of molybdenum were prepared by the different steel certified reference materials in a 50 mL volumetric flask. Add 4 mL of 50 % (v/v) solution of sulphuric acid, 10 mL of 17 % (v/v) solution of perchloric acid, 10 mL of 100.0 mg mL^{-1} solution of sodium thiocyanate and 10 mL of 100.0 mg mL^{-1} stannous chloride solution, followed make up to the mark with 5 % (v/v) solution of sulphuric acid, mix well and let stand for 15 min. Measure the absorbance at 470 nm against a reagent blank. The absorbance of the complex was proportional to the concentration of molybdenum in the range of 0.11-0.89 % (wt/wt). Plot the amount of molybdenum in the sample solution against absorbance to obtain the calibration graph. The linear regression equation for molybdenum was $A = 0.90775C + 0.01547$, $R^2 = 0.9999$ and the relative standard deviation (RSD) was less than 3.0 % (n = 5).

Interference studies: The extent of interference by diverse ions was determined by measuring the absorbance of solutions containing molybdenum and various amounts of diverse ions. The criterion for interference was an absorbance value varying by more than 2 % from the expected value of molybdenum alone. The results show that a large excess of cations and anions which are usually associated in the determination of molybdenum do not interfere. The tolerable amounts in the chromogenic solution of copper, vanadium, cobalt, niobium and chromium for interference were 0.2 mg, 0.05 mg, 0.8 mg, 0.8 mg and 2.4 mg, respectively. Copper when present in excess of equimolar amount increases the absorbance readings and thereby causing positive error. However, copper present in large excess can be removed by extraction with dithizone.

Applications

Determination of molybdenum in X80 pipeline steel: The recommended procedure has been applied satisfactorily to the determination of molybdenum in X80 pipeline steel. The samples were dissolved according to the following procedure: Dissolve 0.2500 g of drilled X80 pipeline steel sample in a mixture of sulphuric acid and phosphoric acid on a 250 mL taper bottle. Continue the treatment with mixture acid till the sample goes into solution and heat to fumes of oxides of nitrogen, sulphuric acid and evaporate almost to dryness. Cool the solution, add 20 mL deionized water. Finally, dilute the solution to 100 mL in a volumetric flask with deionized water. Then, transfer 10 mL of the above stock solution in a 50 mL volumetric flask. Add 4 mL of 50 % (v/v) solution of sulphuric acid, 10 mL of 17 % (v/v) solution of perchloric acid, 10 mL of 100.0 mg mL^{-1} solution of sodium thiocyanate and 10 mL of 100.0 mg mL^{-1} stannous chloride solution, followed make up to the mark with 5 % (v/v) solution of sulphuric acid, mix well and left for 15 min. Measure the absorbance at 470 nm against a reagent blank. The results were summarized in Table-1 with the good accuracy and precision. To verify the results obtained by the proposed method, inductively coupled plasma atomic emission spectrophotometry method was applied to determine the samples according to the literature and the results obtained by the proposed method agreed well with that for the reference method.

TABLE-1
RESULTS OF DETERMINATION OF MOLYBDENUM IN X80 PIPELINE STEEL (ω, n=5)

Sample No.	A	RSD (%)	Content (%)	
			Proposed method	ICP-AES
20108001	0.2159	2.10	0.22	0.23
20108002	0.2696	1.25	0.28	0.27
20108003	0.2520	1.74	0.26	0.26
20108004	0.2161	2.00	0.22	0.22
20108005	0.2501	1.55	0.26	0.25
20108006	0.2424	0.79	0.25	0.27
20108007	0.2375	0.65	0.24	0.25
20108008	0.2443	1.02	0.25	0.25
20108009	0.2152	2.30	0.22	0.21
20108010	0.2239	0.72	0.23	0.23
20108011	0.2376	1.16	0.24	0.22
20108012	0.2711	1.68	0.28	0.28
20108013	0.2163	1.22	0.22	0.23

Determination of molybdenum in X70 pipeline steel: The proposed method was also applied successfully to the determination of molybdenum in X70 pipeline steel. Weigh accurately 0.2500 g of drilled X70 pipeline steel sample and dissolve the sample in mixture of sulphuric acid and phosphoric acid on a 250 mL taper bottle. Then, the chromogenic solution of molybdenum was prepared by the general procedure, which was described above. Measure the absorbance for determination the amounts of molybdenum using the recommended calibration graph and the results were given in Table-2. The concentrations of molybdenum determined by the proposed spectrophotometric method were compared with the concentrations of the samples from the inductively coupled plasma atomic emission spectrophotometry method and a good agreement was obtained.

TABLE-2
RESULTS OF DETERMINATION OF MOLYBDENUM IN X70 PIPELINE STEEL (ω, n = 5)

Sample No.	A	RSD (%)	Content (%)	
			Proposed method	ICP-AES
20107001	0.1711	0.91	0.17	0.17
20107002	0.1734	0.78	0.17	0.18
20107003	0.1268	1.64	0.12	0.14
20107004	0.1245	1.30	0.12	0.12
20107005	0.2411	0.72	0.25	0.24
20107006	0.1684	1.88	0.17	0.17
20107007	0.1789	0.79	0.18	0.18
20107008	0.1261	2.15	0.12	0.13
20107009	0.2419	1.46	0.25	0.23
20107010	0.1828	1.03	0.18	0.19

Conclusion

Based on the chromogenic reaction between molybdenum(V) and sodium thiocyanate, a highly selective and sensitive spectrophotometric method for determination of molybdenum in high grade pipeline steel was proposed. The orange-red coloured mixed-ligand complex exhibits absorption maximum at 470 nm. The stoichiometry of the complex was $[MoO(SCN)_5]^{2-}$

as shown by Job's method and the molar extinction coefficient (ε) is 1.75×10^4 L mol^{-1} cm^{-1}. The proposed method was free from the interference from a large number of analytical important elements and has been applied satisfactorily to the determination of molybdenum in X80 pipeline steel and X70 pipeline steel samples. Compared with other methods for the determination of molybdenum, this method offers advantages of simplicity, less expensive instrumentation and high selective. The satisfactory performance in the determination of molybdenum in high grade pipeline steel demonstrated that the method was practical and suitable not only for quality control analysis but also for product analysis, confirming the promise for high grade pipeline steel research.

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