

DETERMINATION OF MOLYBDENUM BY FLOW-INJECTION ANALYSIS**Salem A. Barakat,* Tariq Y. Mahmoud**

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Abstract

A spectrophotometric flow injection method for the determination of molybdenum in a variety of samples based on the thiocyanate complex formation is proposed. Effects of Cu(II), acidity, reagent concentration and interfering species were investigated. The method has proved to be rapid (80 samples per hour). The RSD of this method was found to be 0.7%. The detection limit for the determination of Mo in steels was found to be 0.05 ppm and the calibration graph is linear up to 200 ppm. The results agreed with those obtained by atomic absorption spectrometry with standard addition method and with certified values of standard reference samples.

Introduction

FIA-spectrophotometry has been used for the determination of molybdenum in various kinds of samples using different methods. In 1970 R. Fuge reported the use of Technicon Auto Analyzer procedure for the colorimetric determination of molybdenum on the basis of its catalytic action on the potassium iodide- hydrogen peroxide reaction in geological and biological samples.¹ In 1975 molybdenum determination in plant was carried out based on benzoin-monoxime complex formation.² Catalytic determination of molybdenum in plants by flow-injection spectrophotometry has been developed in 1988.³ A cation-exchange resin column is incorporated into the system to remove interfering ions.

FIA-spectrophotometry determination of molybdenum(VI) by extraction with quinolin-8-ol at 385 nm has been developed.⁴ Ultra-trace molybdenum determination in natural, fresh and tap water samples by catalytic spectrophotometry with *o*-phenyldiamine has been developed.⁵ Determination of molybdenum in plants materials by flow-injection analysis was performed in 1978 by thiocyanate method.⁶ Also the determination of molybdenum in steels by flow-injection spectrophotometry based on the thiocyanate method in the range 0.10-4.00%(w/w) has been reported.⁷ In 1988

electrolytic dissolution of steels was used for the determination of molybdenum by the flow-injection spectrophotometric thiocyanate method.⁸

All procedures of thiocyanate method used tin(II) chloride as reducing agent to reduce molybdenum(VI) to molybdenum(V), therefore the iron(II) must be present to obtain optimum color.⁹ The tin-iron presence makes the determination more complicated and less sensitive.

In this work ascorbic acid and Cu(II) have been used as reducing agents. The classical spectrophotometric thiocyanate method often recommended for molybdenum determination in steels is very well improved and modified for the flow-injection analysis in a way which has not been used before.

Experimental

Apparatus

A LABINCO, L52 eight-channel peristaltic pump was used in all experiments. A six-way injection valve was used in all experiments. All the tubes used were standard manifold pumping tubing (BV LABORATORIUM INSTRUMENTS). Tygon tubes were used for the aqueous phase and silicon tubing for flow lines. Absorbancies were measured at 464 nm with UNICAM, HEYIOS ultraviolet-visible spectrophotometer, using 10 mm special optical quartz flow cell.

Reagents and solutions

All the chemicals used were of analytical grade.

A stock solution of 1000 ppm of molybdenum(VI) was prepared by dissolving 1.8401 g of dry ammonium molybdate in distilled water and diluted to liter in a calibrated flask. A 100 mL of 5 ppm, 10 ppm, 20 ppm, 40 ppm, 60 ppm, 80 ppm and 100 ppm were prepared and 1 mL of 0.1% Cu²⁺ as copper sulfate was added to each solution. Ammonium thiocyanate solution 20% (w/v) was prepared by dissolving 50 g of ammonium thiocyanate in 50 mL distilled water and completed to 250 mL with water. Ascorbic acid solution 10% (w/v) was prepared by dissolving 10 g of ascorbic acid in distilled water and diluted to 100 mL. Hydrochloric acid solution 3 M was prepared by diluting 25.5 mL of 11.8 M hydrochloric acid to 100 mL with distilled water. Copper(II)

solution 0.1% (w/v) was prepared by dissolving 0.1 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in distilled water and diluted to 100 mL.

General procedure

Samples and standards were examined using the flow system shown in Figure 1 under the conditions given in Table 1. A typical output for a calibration run is shown in Figure 2.

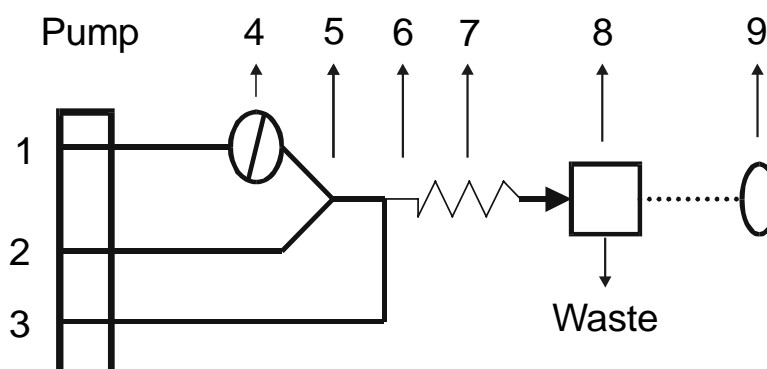


Figure 1. Schematic diagram of the flow-injection system: 1- Ascorbic acid solution 10%; 2- HCl acid solution 3 M; 3- Ammonium thiocyanate solution 20%; 4- Sample injector; 5,6- Mixing points; 7- Mixing coil; 8- Spectrophotometer; 9- Recorder.

Table 1. Conditions for the determination of molybdenum(VI) using flow injection technique.

Reaction coil	0.5 m & 1mm id
Sample injection volume	20 μL
Ascorbic acid solution	0.8 mL / min
Ammonium thiocyanate solution	0.45 mL / min
Hydrochloric acid solution	0.3 mL / min
Aqueous waste	2.1 mL / min

Procedure for steel samples

Dissolve accurately weight sample (containing about 1-10 mg Mo) of steel in 5mL of HCl (1:1) and 15 mL of 70% perchloric acid. Heat the solution until fumes are evolved and then for 6-7 min longer. Cool and add 20 mL of water and warm to dissolve all salts, add 1 mL of 0.1% of copper(II) solution and mix. Dilute the resulting cooled solution to volume in a 100 mL volumetric flask. Measure the peak-height absorbance using the flow system (Figure 1) and the conditions given in Table 1. Evaluate the amount of molybdenum present using a calibration curve. Prepare a calibration curve

over the range (0-100 ppm) of standard molybdenum solution by using 1 mL of 0.1% of copper(II) solution. The results obtained are shown in Table 3.

Results and discussion

Figure 3 shows a calibration curve for the determination of molybdenum in aqueous solutions. The calibration curve obtained was linear over the range 0-200 $\mu\text{g/mL}$ of molybdenum(VI) at 464 nm. The detection limit (3 times base line noise) was 0.05 ppm. The relative standard deviation was 0.7% (10 results) for the determination of 60 ppm molybdenum (Figure 4).

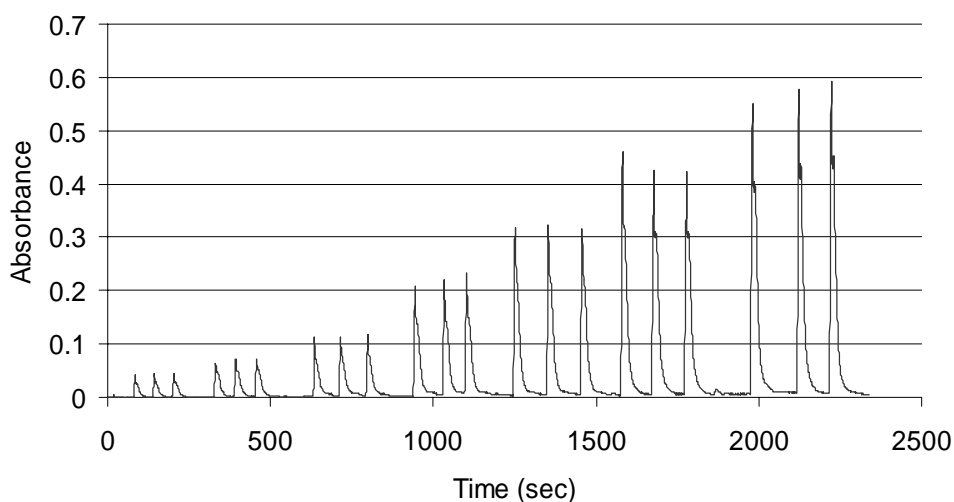


Figure 2. Flow signals obtained for the determination of molybdenum in steel. The peaks correspond to seven standards of 5.00, 10.0, 20.0, 40.0, 60.0, 80.0 and 100.0 ppm molybdenum.

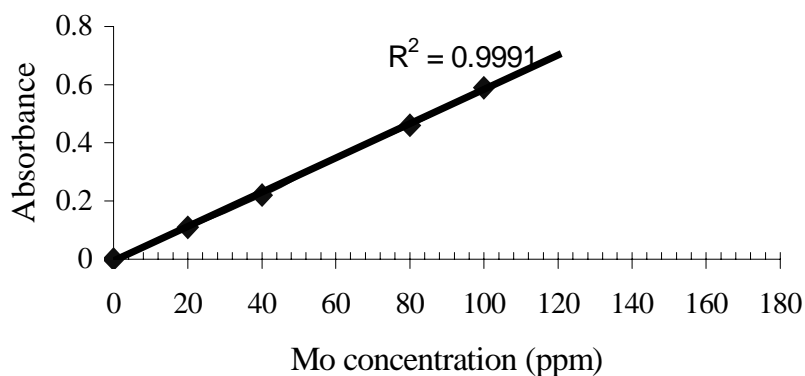


Figure 3. Calibration curve for the determination of molybdenum in water.

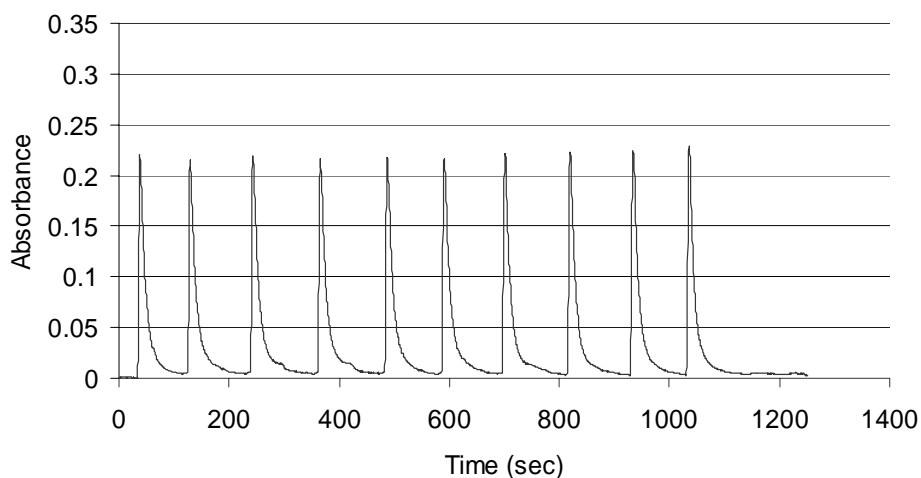


Figure 4. Results of the determination of 60 µg of Mo (n =10).

Effect of copper

Addition Cu(II) improved the development of color of Mo-SCN⁻ in a very short time, i.e., 20 second, therefore this method became applicable to flow-injection analysis (FIA) where ascorbic acid has been used as a reducing agent (weak reducing agent) and 1ml of 0.1% Cu²⁺ was added to 100 mL standard or sample in further work.

Effect of reaction coil

The length of reaction coil was varied from 25 cm to 200 cm. The peak heights were found to be increasing from 25 cm to 40 cm and slightly decreasing at 50 cm to 200 cm. Therefore, 50 cm length was used for routine work (Figure 5).

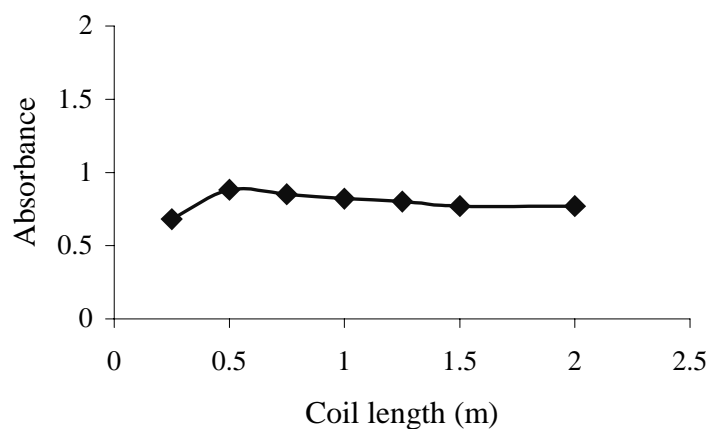


Figure 5. Effect of reaction coil length in meters.

Effect of hydrochloric acid concentration

The acid concentration was varied from 0.5 M to 5 M. The peak heights were found to be constant up to 1 M, (Figure 6). A 3 M acid concentration was used for the further work.

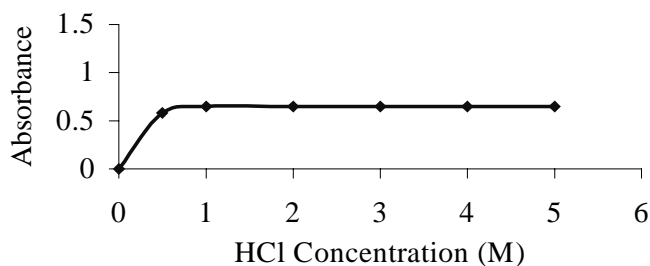


Figure 6. Effect of hydrochloric acid molar concentration.

Effect of different ions

The possible interference of a number of cations and anions were checked for the determination of 50 ppm Mo. The results are summarized in Table 1. Iron(III) was not interfering here because under these conditions iron(III) was reduced to iron(II) which is colorless. Sn(II) decreases the absorbance therefore this method is not valid with compounds containing tin.

Table 2. Effect of different ions on the determination of Mo.

Added as	Ions	Ratio to Mo(V) (w/w)	Relative change (%)
CrCl ₂ ·6H ₂ O	Cr ²⁺	100	no change
CuCl ₂ ·2H ₂ O	Cu ²⁺	100	no change
ZnSO ₄ ·7H ₂ O	Zn ²⁺	100	no change
Co(NO ₃) ₂ ·6H ₂ O	Co ²⁺	100	no change
AlCl ₃	Al ³⁺	100	no change
Cd(NO ₃) ₂ ·4H ₂ O	Cd ²⁺	100	no change
PbCl ₂	Pb ²⁺	100	no change
Ni(NO ₃) ₂ ·6H ₂ O	Ni ²⁺	100	no change
SnCl ₂ ·2H ₂ O	Sn ²⁺	100	-24%
MgCl ₂ ·2H ₂ O	Mg ²⁺	100	no change
FeCl ₃ ·6H ₂ O	Fe ³⁺	100	no change
Na ₂ WO ₄ ·2H ₂ O	W ⁶⁺	100	no change
NaCl	Na ⁺	100	no change
KCl	K ⁺	100	no change
NaF	F ⁻	100	no change
Na ₂ C ₂ O ₄	C ₂ O ₄ ²⁻	100	no change
NaCN	CN ⁻	100	no change

Table 3. Determination of molybdenum in BCS steel.

No	BCS steel No.	Samples mass (g)	Certified value (w/w) (%)	Mo found w/w(%)	Standard deviation
1	407	0.50	0.82	0.801 0.815 0.827	0.009
2	219/3	0.50	0.6	0.582 0.591 0.611	0.012
3	214/2	1.00	0.26	0.259 0.248 0.269	0.0093

Conclusions

A flow-injection procedure is proposed for the determination of molybdenum in many material such as steel based on the thiocyanate method. Effects of copper(II), acidity, reaction coil length and interfering species were investigated by using Flow-injection system. Previous attempts using ascorbic acid as a reducing agent have failed due to the long time required for reduction and color development. The present work has overcome this problem and the developed method showed an enhancement in detection limits and speed of determination. The method is simple to operate and fast (80 injections per hour). The results agreed with certified values of standard reference samples and the detection limits found was 0.05 ppm.

Acknowledgements

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Povzetek

Predlagana je spektrofotometrična injekcijska metoda določevanja molibdena v različnih vzorcih na osnovi nastajanja tiocianatnega kompleksa. Raziskani so bili vplivi Cu(II), kislosti, koncentracije reagenta in drugih motečih zvrsti. Metoda se je pokazala kot hitra (80 vzorcev v eni uri). Ugotovljena RSD metode znaša 0,7%. Meja detekcije pri določevanju Mo v jeklih znaša 0,05 ppm, umeritvena krivulja pa je linearna do 200 ppm. Dobljeni rezultati analize se ujemajo z rezultati analize z atomsko absorpcijsko spektrometrijo po postopku s standardnim dodatkom in s certificiranimi vrednostmi standardnih referenčnih vzorcev.