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The Determination of Molybdenum (VI) concentrations by Flow Injection Analysis Spectrophtometric in Natural Water

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Abstract

A spectrophotometric flow injection method for the determination of molybdenum (VI) in water sample based on thiocynate complex formation was applied. A linear line was obtained over the range 0.02- 0.1 µg/ml of Mo (VI).The RSD of this method was found to be 0.015%, and the detection limit was found to be 0.01 µg/ml. The linear curve has a regression coefficient of 0.9997 with sample throughput 78 sample/h. The influence of interferences on this method was studied. The molybdenum (VI) concentrations in Shatt Al-Arab river has been measured, at each of the five stations over 12 months during the period from October 2009 to September 2010, monthly variations were recorded. The results was showed that Mo (VI) concentrations ranged 0.02-0.095 µg/ml. where these results indicated that the average of molybdenum (VI) in study area increasing from north (Qarmat Ali) to the south (Fao).The results point clearly that the concentrations of Mo (VI) increasing in December 2009,January 2010 and February 2010, especially in station 2 (Ashar) and station 4 (Seeba) which was 0.085-0.095 µg/ml this can be attributed to put waste from industrial sources ,agricultures and human waste and to the waste from Abadan refinery were the molybdenum is valuable catalyst in the refining of petroleum.

Key Words: Flow injection analysis, spectrophotometer, Molybdenum, natural water.

1. Introduction

Flow Injection Analysis (FIA) is one of the most popular continuous – flow technique and its versatility and simplicity can help to bring automation to teaching laboratories. The success of an FIA application is strongly dependent on the manifold design and some experimental details need to be understood to overcome pitfalls [1].

FIA is a very successful method in simplifying chemical assays. The main reasons for the success are the following advantage of FIA over conventional manual techniques: Reduced labour costs due to automation ,Great precision due to mechanical performance of the assays, High sampling rate, smaller sample and reagent consumption and waste generation, simplicity and low cost instrumentation, Availablability of instrumentation in all laboratories, Reduced analysis cost when a lot of samples have to be analyzed, increased precision compared to batch methodologies and Automation in sample preparation and detection [2,3]

Several instrumental techniques can be coupled to FIA. In this sense FIA is often used for sample processing ,for improving precision and sampling rate, and for implementation of less-conventional batch procedure (e.g,mangment of unstable reagents and products). FIA is a useful tool for carrying out chemical reaction. It makes classical procedures more attractive for students[4].

Molybdenum is used in the manufacture of special steels, in electrical contacts, spark plugs, X-ray tubes, filaments, screens and grids for radio valves, and in the production of tungsten, glass-to-metal seals, non-ferrous alloys and pigments. Molybdenum disulfide has unique properties as a lubricant additive. Molybdenum compounds are used in agriculture either for the direct treatment of seeds or in the formulation of fertilizers to prevent molybdenum deficiency. Molybdenum is valuable as a catalyst in the refining of petroleum [5]. The metal is an essential trace element in plant nutrition, Molybdenum forms salts with valencies of 3,4 or 6,but hexavalent are the most stable [6].

Various methods have been developed for quantification of molybdenum(VI) concentration in different samples such as spectrophotometric [7], Flow injection chemiluminescence [8], atomic absorption spectrometry [9], and electrochemical methods [10] Spectrofluorimetry [11], Inductively coupled plasma mass spectrometry [12].

The aim of the present work is to establish sufficient conditions for flow injection spectrophotometric method for the determination of Mo (VI) concentrations in water of Shatt Al-Arab river.

2. Materials and methods

2.1 Study area and sampling

Shatt Al-Arab river is the main source for fresh water in southern Iraq .Shatt Al-Arab River originates from the junction of Tigris and Euphrates rivers at Qurna.The length of this river is about 175 km; its width varies from 0.4km at Basrah city to 1.5 km at the river mouth in Fao. A total of 96 samples of natural water of Shatt al-Arab River were collected from five stations Qarmat Ali, Ashar , Abu Al-khaseeb , Al-Seeba and Fao as they as shown in Figure (1) and Table (1) for 12 months during the period from October 2009 to September 2010. Water sampler was used to collect undersurface water samples for chemical analysis and 1ml of concentrated nitric acid was added to each sample [13].The samples were transported to laboratory in a cool box. The stations are selected in such manner to evaluate the molybdenum (VI) levels in the study area.

2.2 Reagents

All the chemicals used were of analytical grade. A stock solution of 1000 µg/ml of molybdenum(VI) was prepared by dissolving 1.8401 g of dry ammonium molybdate in distilled water and diluted to one liter. A 100 mL of 0.02,0.04,0.06,0.08 and 0.1 µg/ml were prepared and 1mL of 0.1% Cu^{2+} as copper sulfate was added to each solution. Ammonium thiocyanate solution 20% (w/v) was prepared by dissolving 50 g of ammonium thiocyanate in 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 0.2% (w/v) was prepared by dissolving 0.2 g of $CuSO_4.5H_2$

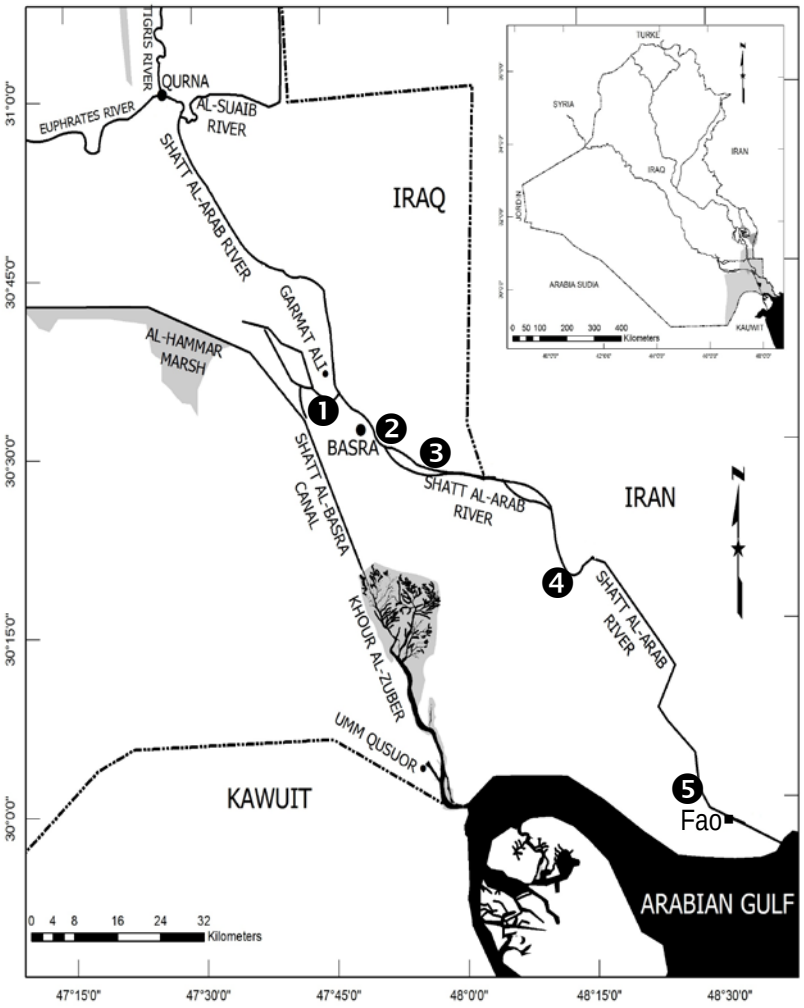


Fig. (1) The Location map of the study area showing the sampling stations

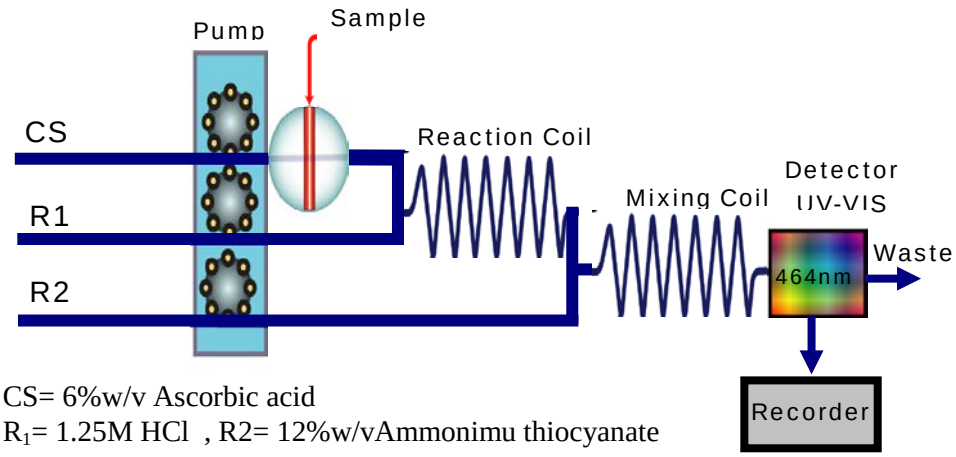
Table (1) : Sampling sites, Names and positions of Study area.

Stations	Sampling Point Name	Latitude	Longitude
St.1	Qarmat Ali	30°34'514"N	47°44'684"E
St.2	Ashar	30°31'169"N	47°50'647"E
St.3	Abu Al-khaseeb	30°27'709"N	48°00'633"E
St.4	Al-Seeba	30°20'210"N	48°15'995"E
St.5	Fao	29°59'359"N	48°27'792"E

2.3 Flow Injection Analysis system

A schematic diagram of a home-made flow injection (FIA) system established in marine science center-marine chemistry department as shown in figure 2. A peristalatic pump (Auto-analyzer) with constant speed (16.7 cycle/min) was used for propelling a carrier solution (CS) and a reagent solutions ($R_1$and R_2).A six- way valve (RHEODYNE,Catati,California,USA) was used for introducing the standards and samples into the carrier stream.

The absorbance was measured with spectrophotometer (shimadzu,UV-150.Japan) equipped with 200µl flow cell (QS-Hellma) and the Peak heights were recorded with a chart recorder (SIEMENS, Kompensograph).Teflon tube (0.5mm i.d) was used throughout the remainder of the manifold. All results are the mean of six injections of the natural water samples. O
in distilled water and diluted to 100 mL.

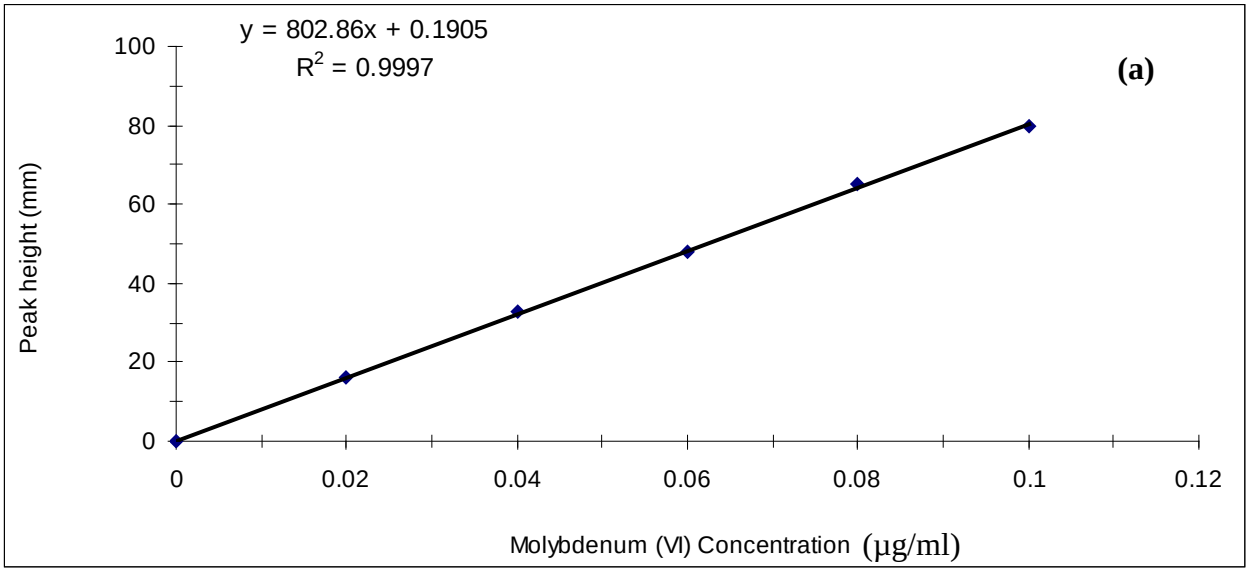


CS= 6%w/v Ascorbic acid
R_1= 1.25M HCl , R2= 12%w/vAmmonimu thiocyanate

Fig.2 The FIA manifold for the determination of Molybdenum (VI) in natural water.

3. Results and discussion

Figure 3 shows a calibration curve for the determination of molybdenum (VI) in natural water of Shatt Al-Arab river. The calibration curve obtained was linear over the range 0.02-0.1 µg/ml of molybdenum(VI) at 464 nm. The detection limit (2×noise) was 0.01 µg/ml. The relative standard deviation for ten replicates of (0.1 µg/ml) molybdenum (VI) was 0.015%. The linear graph has a regression coefficient of 0.9997 and the sample throughput was 78 sample/h.



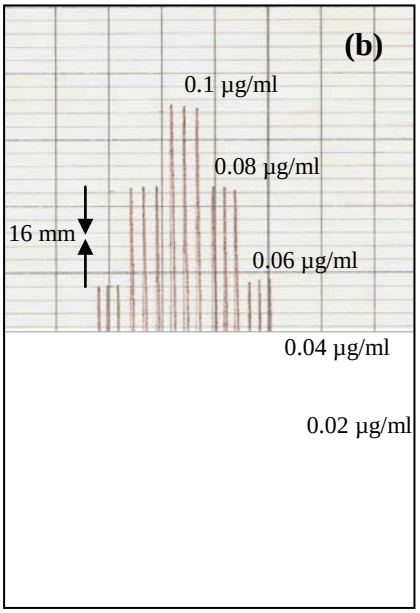


Fig.3 (a) The standard calibration graph for Molybdenum (VI) determination.
(b) Peaks obtained by injected Mo (VI) Standard.

The following parameters effecting the performance of molybdenum (VI) determination in natural water with FI system were investigated:

The Effect of Sample volume:

The effect of sample volume on the peak height is shown in Fig. 4. The maximum peak height was obtained with the injection of 200 µl (0.1µg/ml) molybdenum (VI),therefore 100 µl was used as injection in subsequent experiments.

The Effect of reaction coil:

Fig.5 shows the effect of reaction coil length on peak height for 0.1µg/ml molybdenum (VI). The length of reaction coil was varied from 20 cm to 90 cm. The results show that the peak height increases with the increasing of reaction coil length Therefore, 60 cm length was used in subsequent experiments.

The Effect of flow rate and Total flow rate

The effect of flow rate and total flow rate on peak height of 0.1 µg/ml molybdenum (VI) in the range 0.45-2.0 ml/min and 1- 4 ml/min respectively, were shown in figures 6 and 7. It was found that 1.20 and 2.4 ml/min flow rate for carrier stream and total flow rate were the best, so they were used in subsequent work.

The Effect of Ascorbic Acid concentration (%w/v)

The influence of the ascorbic acid concentration on the peak height for 0.1 µg/ml molybdenum (VI) is shown in fig.8. The increase of peak height is due to the increase of ascorbic acid concentration to more complex formed. A above 6%w/v, the peak height decreased, therefor 6%w/v ascorbic acid was used in subsequent experiments.

The Effect of hydrochloric acid concentration (M)

Fig.(9) indicates that peak height increases with the increasing of hydrochloric acid concentration. So,1.25 M is the best concentration to be optimized.

The Effect of Ammonium thiocyanate concentration (%w/v)

The influence of Ammonium thiocyanate concentration on the peak height for 100 µl of 0.1 µg/ml molybdenum (VI) is shown in Fig.10 .The peak height increases with increasing the concentration of Ammonium thiocyanate which thought to be due to more complex formation. A above 12%w/v the peak height decreases.Thus 12%w/v Ammonium thiocyanate was used in subsequent experiments.

The Effect of copper (II)

Fig. (11) indicates that addition of 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, and 1ml of 0.1% Cu^{2+} was added to standard or sample in subsequent experiments.

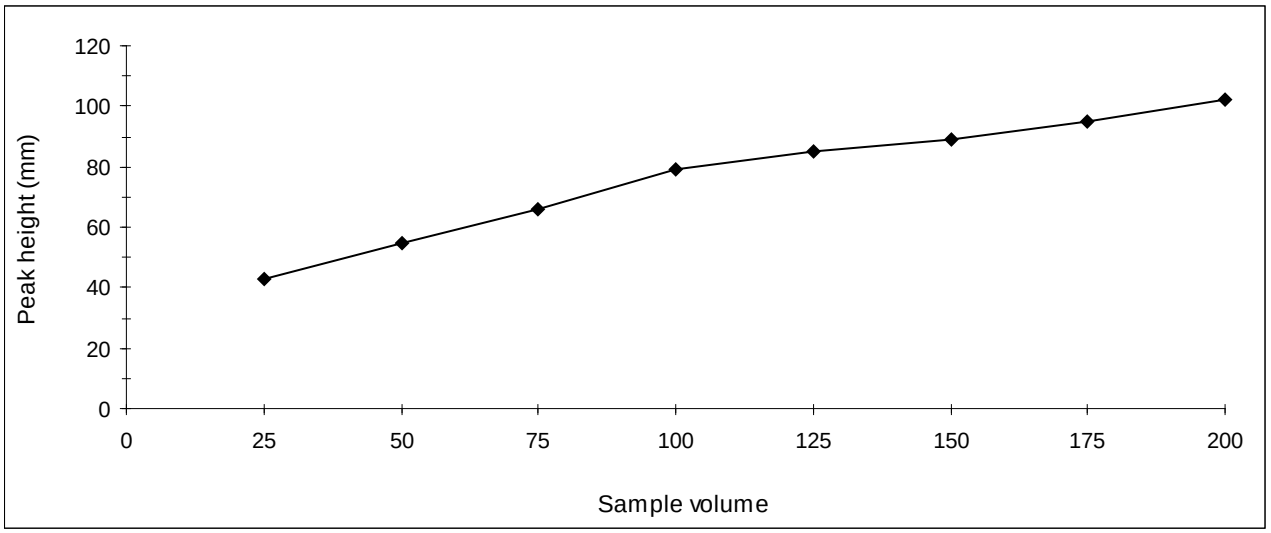


Fig.4 The effect of sample volume on the peak height for 0.1µg/ml molybdenum (VI)

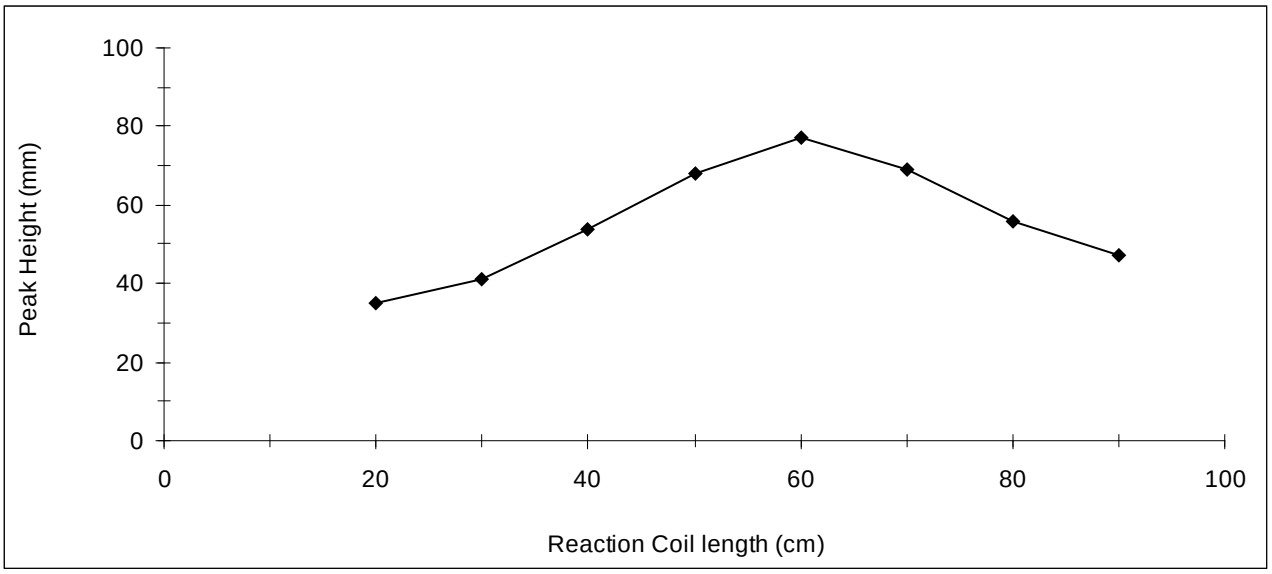


Fig.5 The Effect of reaction coil length on the peak height for 0.1µg/ml molybdenum (VI)

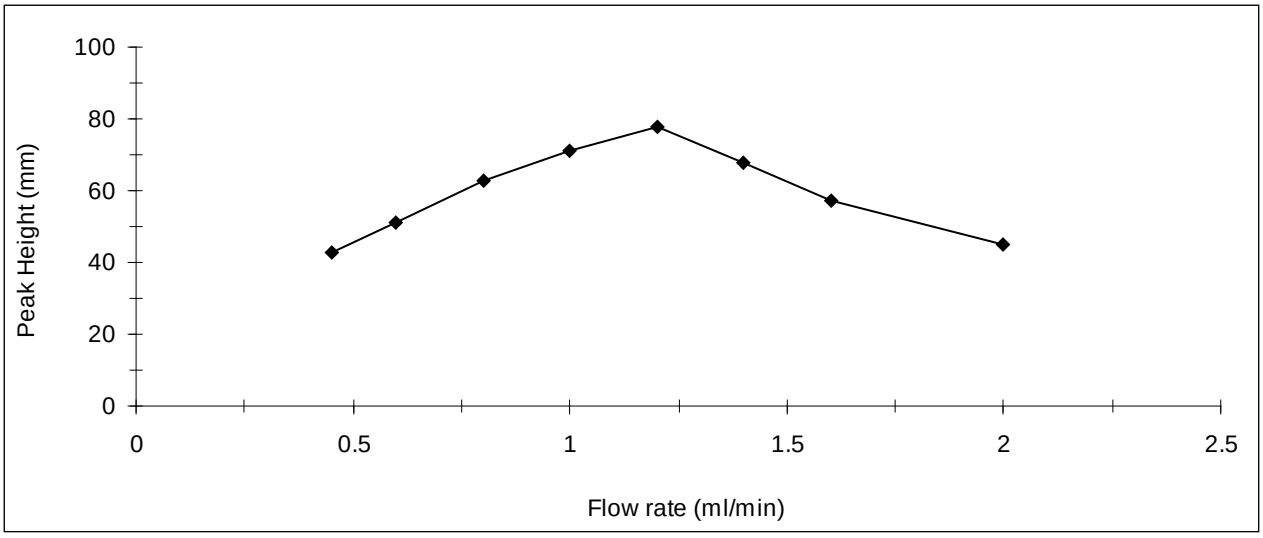


Fig.6 The Effect of flow rate on the peak height for 0.1µg/ml molybdenum (VI)

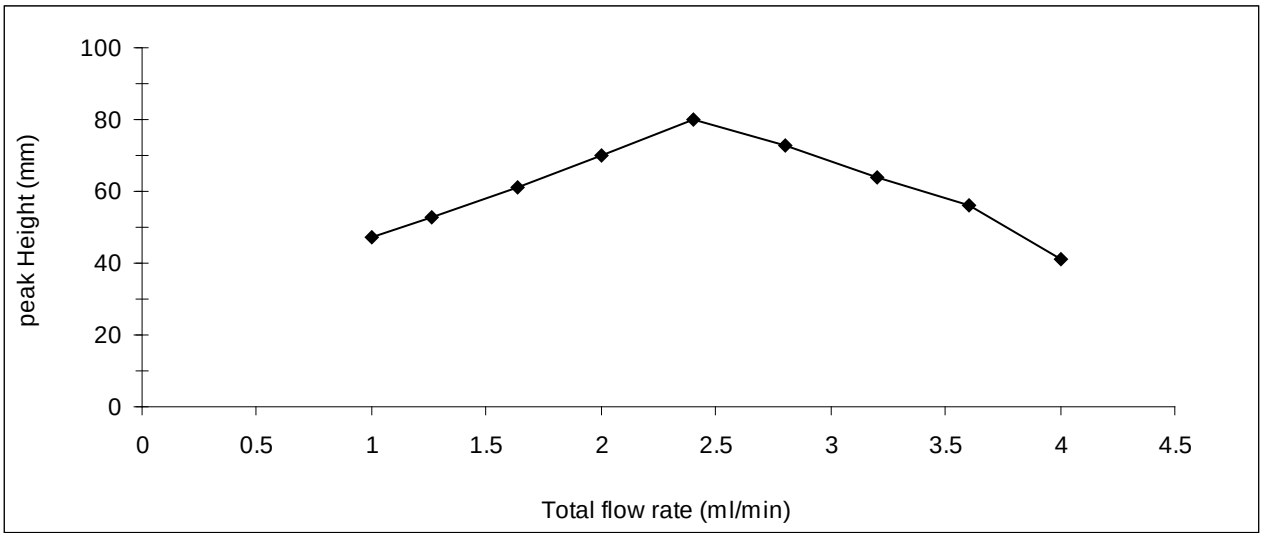


Fig.7 The Effect of total flow rate on the peak height for 0.1µg/ml molybdenum (VI)

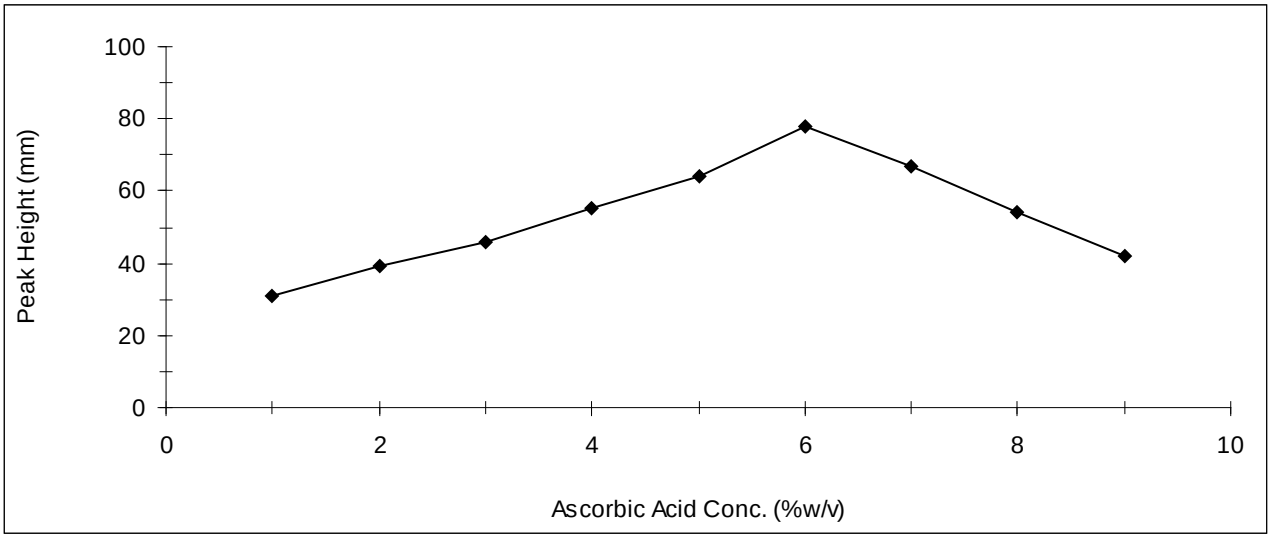


Fig.8 The Effect of Ascorbic acid conc. on the peak height for 0.1µg/ml molybdenum (VI)

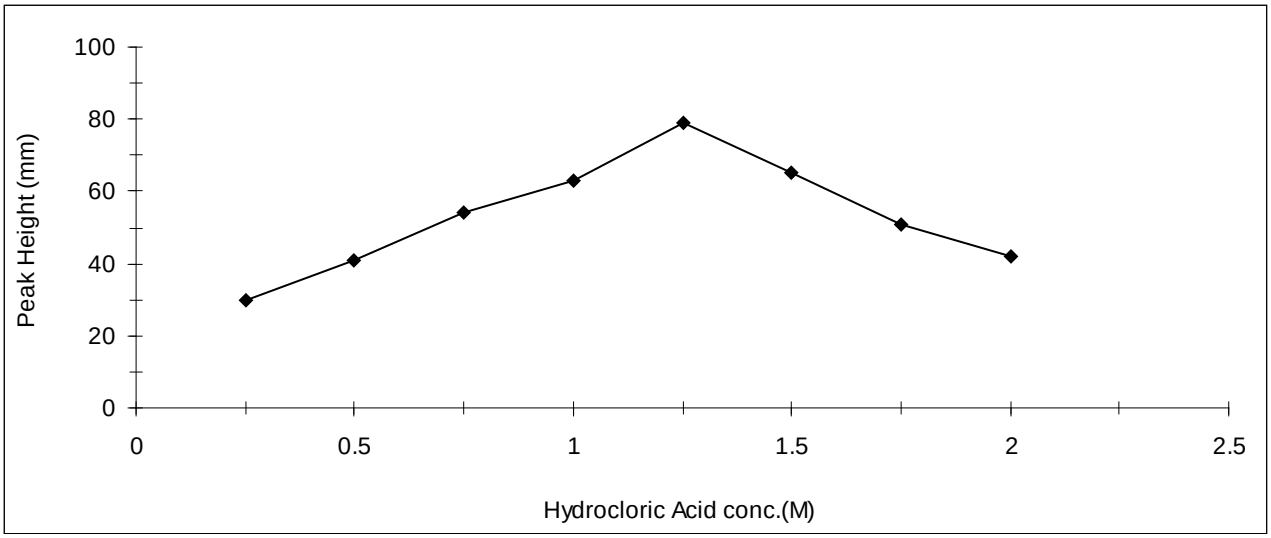


Fig.9 The Effect of hydrochloric acid conc. on the peak height for 0.1µg/ml molybdenum (VI)

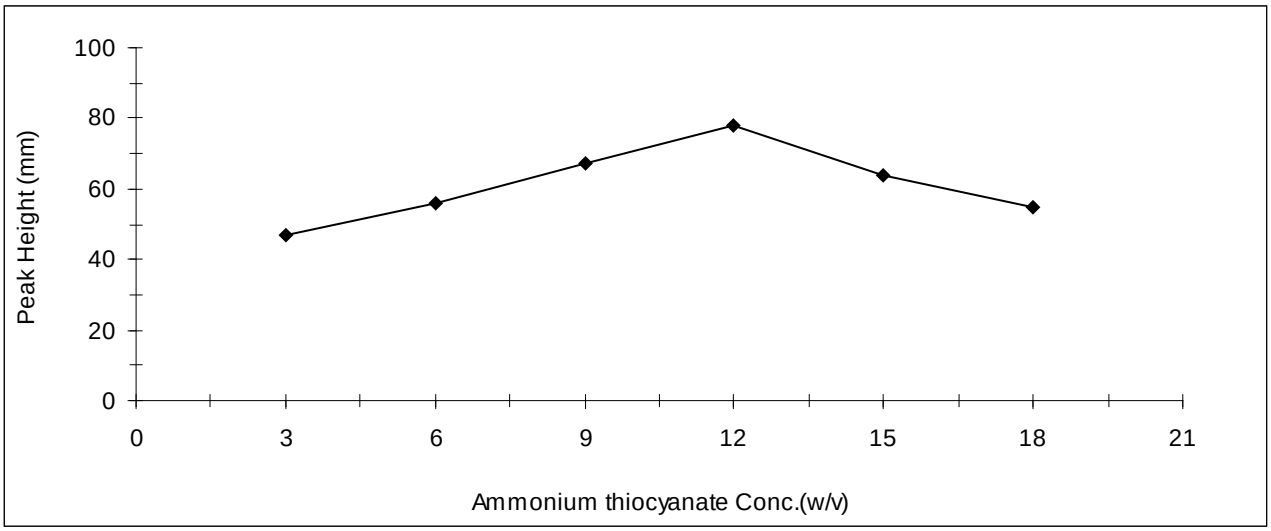


Fig.10 The Effect of Ammonium thiocyanate conc. on the peak height for 0.1µg/ml molybdenum (VI).

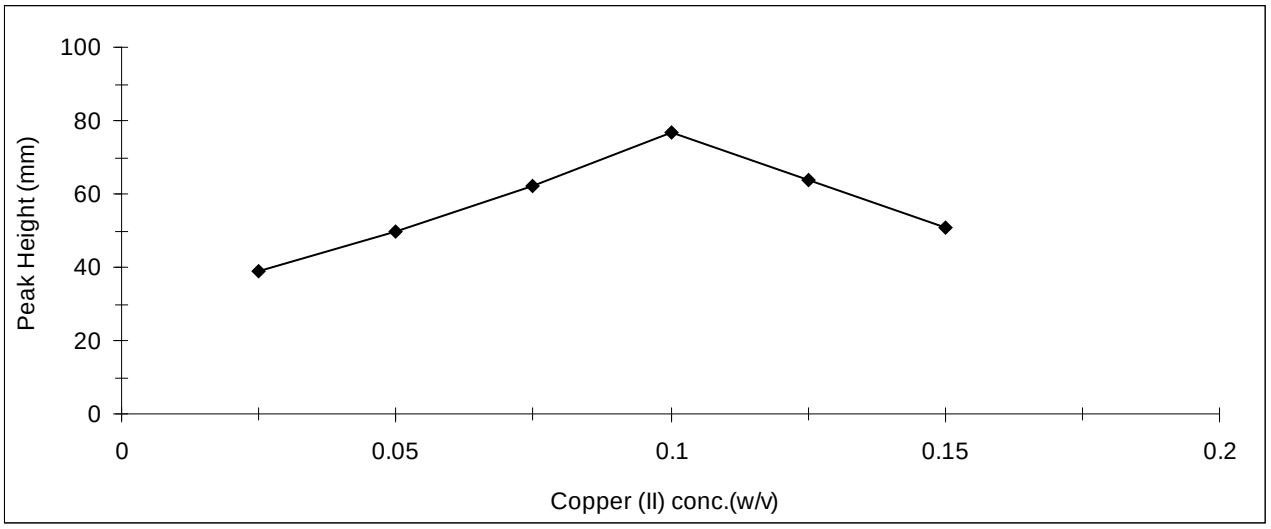


Fig.11 The Effect of Copper (II) on the peak height for 0.1µg/ml molybdenum (VI).

4. The effect of different ions

The possible interference of a number of cations and anions were checked for the determination of Mo (Table 2). The results showed that excess of ions are not interfering on determination of molybdenum. 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 Sn [14].

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

No.	Added as	Ions	Relative change (%)
1	$CuCl_2.2H_2O$	Cu^{2+}	no change
2	$ZnSO_4.7H_2O$	Zn^{2+}	no change
3	$AlCl_3$	Al^{3+}	no change
4	$Ni(NO_3)_2.6H_2O$	Ni^{2+}	no change
5	$SnCl_2.2H_2O$	Sn^{2+}	-36%
6	$MgCl_2.2H_2O$	Mg^{2+}	no change
7	$FeCl_3.6H_2O$	Fe^{3+}	no change
8	NaCl	Na^{+}	no change
9	KCl	K^{+}	no change

5. The molybdenum (VI) in Shatt al-Arab water:

There are mainly different sources of pollutants in aquatic environment, such as, organic materials, major ions and trace metals. They contribute to different sources as natural or anthropogenic. Some natural sources include storm dust-fall, erosion or crustal weathering as well as dead and decomposed biota in water, whereas the anthropogenic sources include sewage, industrial, agricultural and automobile waste in addition to shipwrecks and dumping of war materials. [15,16]. Molybdenum compounds are used in agriculture either for the direct treatment of seeds or in the formulation of fertilizers to prevent molybdenum deficiency.

Table (3) Concentrations levels of Molybdenum (VI) µg/ml in Shatt Al-Arab water

Stations	Oct. 2009	Nov. 2009	Dec. 2009	Jan. 2010	Feb. 2010	Mar. 2010	Apr. 2010	May. 2010	Jun. 2010	Jul. 2010	Aug, 2010	Sep. 2010	Avrg.
Qarmat Ali	0.04	0.055	0.06	0.055	0.045	0.025	0.025	0.03	0.02	0.03	0.035	0.035	0.03
Ashar	0.075	0.09	0.095	0.085	0.09	0.07	0.080	0.065	0.06	0.055	0.03	0.045	0.07
Abu Al-Kaseeb	0.065	0.05	0.07	0.07	0.065	0.04	0.030	0.025	0.04	0.04	0.045	0.04	0.04
Seeba	0.085	0.09	0.095	0.095	0.095	0.065	0.070	0.045	0.045	0.050	0.065	0.060	0.07
Fao	0.08	0.085	0.085	0.075	0.08	0.04	0.050	0.045	0.055	0.040	0.040	0.035	0.05

Table (3) and Figure (12) show the monthly variations of molybdenum concentrations in shatt Al-Arab water. These results indicated that the average of molybdenum (VI) in study area increasing from north (Qarmat Ali) to the south (Fao). The results showed that molybdenum (VI) concentration decreasing in stations 1 (Qarmat Ali) during the study period.

The results point clearly that the concentrations of Mo (VI) increasing in December 2009,January 2010 and February 2010, especially in station 2 (Ashar) which was 0.095,0.085,0.09 µg/ml, respectively, this can be attributed to put waste from industrial sources ,agricultures and human waste. and also, it is clear that the concentrations of Mo (VI) in station 4 (seeba) recorded the maximum values ,this can be attributed to the waste from Abadan refinery were the molybdenum is valuable catalyst in the refining of petroleum, while during March, April, May, and Jun 2010 in all stations the levels were low which could be explained due to the effect of temperature where oils would decompose and water flushing following the

increase activity of human beings [17].The Concentrations of trace metals in river water levels are affected by change of discharge during the year where they get early spring discharges leading to proliferation and there by reduce water discharges which leads to decreased concentration of environmental pollutants The study showed low concentrations Molybdnium changes during this period

So, in general the average of molybdenum (VI) concentrations in Shatt Al-Arab water which is the main source of drinking water in Basrah province higher than the concentrations limit (0.07 µg/ml) as reported in the world Health Organization [19].

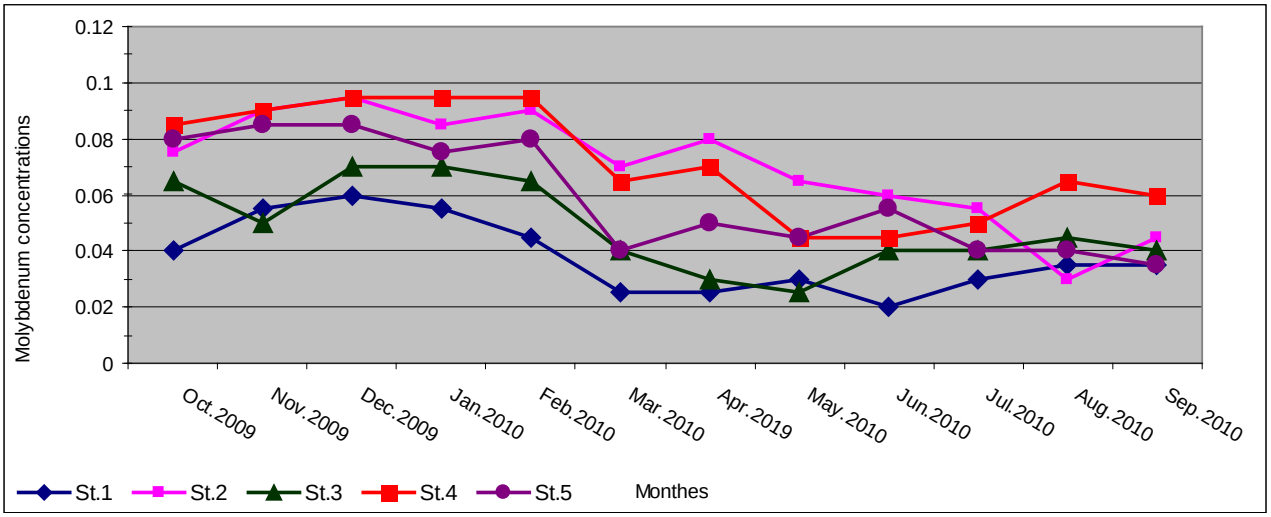


Fig (12) The seasonal variations for Mo (VI) concentrations in Shatt Al-Arab water.

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