Arabian Journal of Chemistry (2016) 9, S1105–S1109

King Saud University

Arabian Journal of Chemistry

www.ksu.edu.sa
www.sciencedirect.com

ORIGINAL ARTICLE

Catalytic spectrophotometric determination of Mo(VI) in water samples using 4-amino-3-hydroxy-naphthalene sulfonic acid

Abdolreza Iraj Mansouri [a,*], Mohammad Mirzaei [b,1], Daryoush Afzali [b,1], Farideh Ganjavie [c,2]

[a] *Material Department, Research Institute of Materials, International Center for Science, High Technology & Environmental Sciences, Kerman, Iran*
[b] *Environment Department, Research Institute of Environmental Sciences, International Center for Science, High Technology & Environmental Sciences, Kerman, Iran*
[c] *Department of Chemistry, Faculty of Science, Kerman Branch, Islamic Azad University Kerman, Iran*

Received 3 August 2011; accepted 10 December 2011
Available online 20 December 2011

KEYWORDS

Molybdenum determination;
Water analysis;
Catalytic spectrophotometry;
4-Amino-3-hydroxy-naphthalenesulfonic acid

Abstract In the present work, a sensitive, and simple kinetic method was developed for the determination of trace amounts of Mo(VI) based on its catalytic effect on the oxidation of 4-Amino-3-hydroxy-naphthalenesulfonic acid (AHNA) with H_2O_2. To optimize the parameters affecting the aforementioned system, the reaction was followed spectrophotometrically by tracing the oxidized product at 475 nm. The absorption of the solution in the presence and absence of the molybdenum ion in different conditions was compared. The optimum reaction conditions were: 9 mmol L^{-1} AHNA, 35 mmol L^{-1} H_2O_2, 27 mmol L^{-1} acetate buffer with pH = 5.3 at temperature 40 °C for 30 min. A 0.02% (w/v) di-ethylene tri-amine penta acetic acid (DTPA) was used as a masking reagent for confirming selectivity. The calibration curve was linear in the range 0.1–4.0 ng mL^{-1}

---

* Corresponding author. Tel.: +98 3426226611–13; fax: +98 3426226617.
E-mail addresses: mansouri_ai@yahoo.com (A.I. Mansouri), m_mirzaei36@yahoo.com (M. Mirzaei), daryoush_afzali@yahoo.com (D. Afzali), farideh_ganjavie@yahoo.com (F. Ganjavie).
[1] Tel.: +98 3426226611–13; fax: +98 3426226617.
[2] Tel.: +98 3413210041–50; fax: +98 3413210051.

Peer review under responsibility of King Saud University.

Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.arabjc.2011.12.009

with a correlation coefficient of 0.999 and the detection limit was 0.04 ng mL^{-1} ($n = 15$) based on the $3\sigma_{bl}/m$. The proposed method was used for the determination of molybdenum in the different water and waste water samples.

1. Introduction

Molybdenum is an essential trace element for both animals and plants. In animals, it is a component of xanthine oxidase and other redox enzymes. In plants, this element is necessary for the fixation of atmospheric nitrogen by bacteria to begin the protein synthesis. Deficiency or excess of molybdenum can cause damage to plants, and hence its routine control is highly recommended for healthy plant growth (Shrives et al., 2009). Molybdenum is added in trace amounts of fertilizers to stimulate plant growth. Molybdenum is also used as a component in glass, catalyst, lubricant and alloy of steel, owing to its high melting point, high strength at higher temperatures, good corrosion resistance and high thermal conductivity (Pyrzynska, 2007). However, high concentration of Mo(VI) may be toxic for humans, plants and animals. Molybdenum is widely used in a variety of industrial processes. The U.S. EPA drinking water health advisories recommended longer term limits of 10 ng mL $^{-1}$ for children and 50 ng mL^{-1} for adults and the United Nations Food and Agriculture Organization recommended a maximum level of 10 ng mL^{-1} for irrigation water (Mubarak et al., 2007). Since the concentration (FAO) of molybdenum in plants, water and soil is generally considered as parts per billion levels, a sufficient sensitivity method is required for the determination of molybdenum (Zarei et al., 2006). Several techniques such as neutron activation analysis (Danko and Dybczynski, 1997; Sun et al., 1999), flame atomic absorption spectrometry (FAAS) (Greenberg et al., 2000; Carrion et al., 1986; Resende-Boaventura et al., 1994), electro thermal atomic absorption spectrometry (ETAAS) (Burguera et al., 2002; Ferreira et al., 2003), Inductively coupled plasma mass spectrometry (ICP-MS) (Reid et al., 2008), adsorptive stripping voltammetry (Tyszczuk and Korolczuk, 2008), differential pulse polarography (Puri et al., 1998) and spectrophotometry (Soylak et al., 1996), have been reported for the determination of molybdenum. Preconcentration and separation of molybdenum is necessary in order to detect trace levels of analyte and subsequently eliminate the interference present in the sample (Soylak et al., 1997).

Spectrophotometric methods based on the catalytic effect of Mo(VI) are very sensitive. Catalytic spectrophotometric methods offer low cost, simple and sensitive alternative for the determination of trace levels of molybdenum (Mubarak et al., 2007). These methods were selected based on its catalytic effect on the oxidation (or reduction) of a substrate with a suitable oxidant (or reductant) such as chlorate (Mubarak et al., 2007). Periodate (Rezaei and Majidi, 2007), hydrogen peroxide (Xiong et al., 2007; Yatsimirskii and Afanasva, 1956), hydrazine hydrochloride (Mousavi and Karami, 2000), or stannous chloride (Jonnalagadda and Dumba, 1993). However, the limited sensitivity and/or selectivity are common disadvantages (Mubarak et al., 2007). One of the applications of AHNA to catalytic analysis was the determination of 0.5–4.0 ng mL^{-1} Cu(II); where under optimum conditions, relative errors were reported 10–19%.

The aim of this study is to develop a sensitive and simple method for determination of trace amounts of Mo(VI) in aqueous samples by catalytic spectrophotometry method without separation and preconcentration. The method was conveniently applied for the determination of Mo(VI) in different water and waste water samples.

2. Experimental

2.1. Apparatus

Absorbance measurements were performed on a Cary 500 scan UV–VIS–NIR spectrophotometer (Varian, Australia), equipped with a Cary temperature controller used to deliver accurate volumes. pH measurements, with an accuracy of ±0.1, were made on a calibrated Metrohm pH meter model 691 (Metrohm, Switzerland). All glassware and storage bottles were soaked in 10% HNO_3 overnight and thoroughly rinsed with water prior to use.

2.2. Reagents

All chemicals were of pure analytical grade and were purchased from Merck (Darmstadt, Germany) and Aldrich (Milwaukee, WI, USA). A stock standard solution of 1000.0 μg mL^{-1} Mo(VI) from Caledoni Laboratories LTD. (Georgetown, Ont., Canada) was also provided. Working standard Mo(VI) solutions were daily prepared from their respective stocks. A 0.75 mol L^{-1} hydrogen peroxide from Merck solution was daily prepared from the standardized stock solution. A working acetate buffer solution was prepared

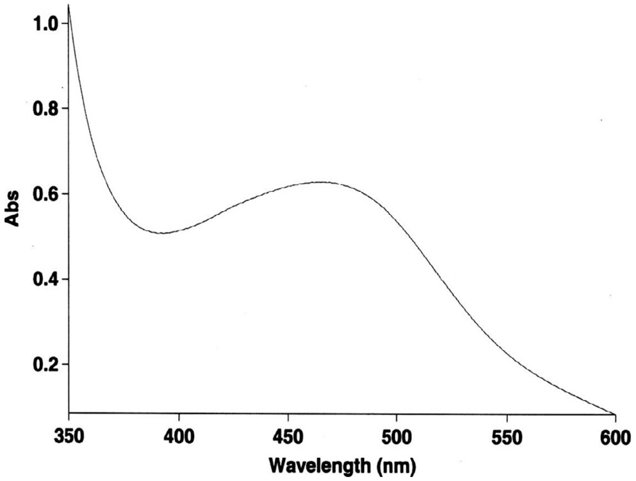

Figure 1 Absorption spectra for the oxidation of 9 mmol L^{-1}AHNA with 35 mmol L^{-1} H_2O_2 and 27 mmol L^{-1} buffer with pH 5.3, following the recommended procedure, in the presence of 2.0 ng mL^{-1} Mo(VI).

by adjusting the pH of 180 mL of 2.0 mol L^{-1} Aristar grade acetic acid from Aldrich with supra pure NaOH from Merck to a pH of 5.3 ± 0.1 and diluting in a 200 mL volumetric flask. A working solution of 30 mmol L^{-1} of AHNA from Aldrich was prepared every 48 h by dissolving 0.236 g of Na_2SO_3 from Merck and 30 mg of DTPA from Merck in about 40 mL of water and 0.360 g AHNA. The resulted solution was diluted by water in a 50 mL volumetric flask, wrapped with an aluminum foil and kept at room temperature.

2.3. Sampling

Water samples including well water, tap water, waste water, geothermal water and mineral water were collected from different regions (Mahan, Bardsir, Sirch, Sarchashmeh and Kerman) in Kerman province, Iran. All water samples were kept in acid leached polyethylene vial. Before the analysis, the organic content of the water samples was oxidized in the presence of 2 mL 1% $HClO_4$ and then 1 mL concentrated nitric acid was added to 1 L of water samples. These water samples were filtered through a cellulose membrane filter (Millipore) of pore size 0.45 μm to remove particulate matter. The pH of the filtered water samples was adjusted to approximately 5.3 using acetate buffer solution.

2.4. Recommended producer for the determination Mo(VI)

The working H_2O_2 solution was kept at 40 °C in thermostated water bath. About of 1.9 mL of the sample solutions was transferred to one of the thermostatic spectrophotometric cells

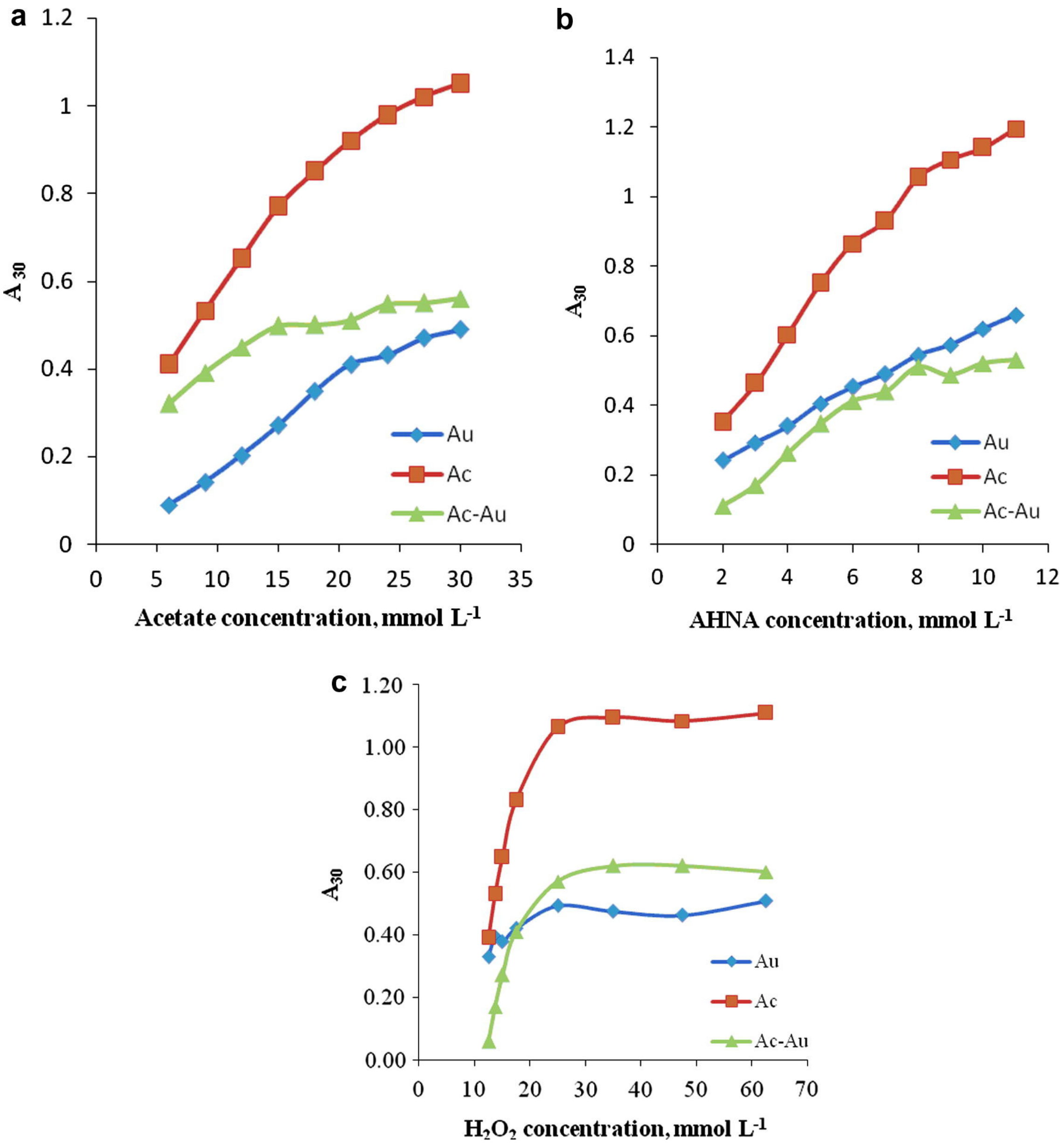

Figure 2 Effects of reaction variable conditions were those given in the recommended procedure. Uncatalyzed reaction (A_u) (a), reaction catalyzed by 2 ng mL^{-1} Mo(VI) (A_c) (b), the reaction sensitivity (A_c–A_u) (c).

Table 1 Analysis of molybdenum ion in water samples.

Sample	Added (ng mL^{-1})	Found (ng mL^{-1})	Recovery (%)
Well water (Mahan)	0	0.170 ± 0.003	–
	0.25	0.416 ± 0.008	98.3
Tap water (Mahan)	0	0.233 ± 0.005	–
	0.25	0.475 ± 0.010	96.8
Tap water (Kerman)	0	0.274 ± 0.007	–
	0.25	0.538 ± 0.010	105.6
Wastewater (Copper Factory, Sarchashmeh, Rafsanjan)	0	0.446 ± 0.012	–
	0.25	0.693 ± 0.014	98.8
Geothermal water (Sirch, Kerman)	0	3.160 ± 0.047	–
	0.25	3.421 ± 0.078	104.4
Mineral water (Bardsir, Kerman)	0	0.590 ± 0.016	–
	0.25	0.832 ± 0.015	96.8

Mean ± standard deviation ($n = 3$).

with adding to it, 0.9 mL of the working AHNA solution. The procedure was followed by leaving 45.0 μL of the working acetate buffer having pH 5.3 and the reacting mixture in the thermostatic cell for 10 min at 40 °C in order to reach the equilibrium temperature (Mubarak et al., 2007). Then 140.0 μL of the working H_2O_2 solution was added to shake well and the absorbance was recorded at 475 nm after 30 min against water as a reference. The dissolved Mo(VI) concentration of the unknown sample was determined from a calibration graph, similarly to the one prepared with the working standard Mo(VI) solution.

3. Results and discussions

3.1. Preliminary consideration

The oxidation of AHNA with H_2O_2 is a slow process that can be catalyzed by Cu(II); where Cr(VI), Fe(III), Fe(II), and Mo(VI) ions are seriously interfered (Mubarak et al., 2007). The yellow-orange oxidized product exhibited one absorption band in the visible range of the spectrum (Fig. 1). The position of λ_{max} was slightly shifted to longer wavelengths by increasing the standing time after mixing the reagents up to 25 min; thereafter, it remained fixed at 475 nm for at least 90 min. Therefore, fixed time measurements after 30 min of mixing the reagents at 475 nm were adopted for further optimizations. Preliminary experiments showed that AHNA is almost insoluble in water and/or mineral acids; however, it dissolves easily in alkaline solutions. Such solutions are completely unstable and readily darken after preparation because of the rapid auto-oxidation of AHNA catalyzed by ultra-trace amounts of ions that may be found in these solutions. Therefore, in the present work, AHNA was dissolved in sodium sulfite as a stabilizer in the presence of DTPA as a masking agent that effectively gave stable AHNA solutions and this procedure eliminated the rapid auto-oxidation of the reagent. It was found that the reaction sensitivity for Mo(VI) determination in the reaction cell was not affected by the presence of up to 0.03% (w/v) sulfite and 0.003% (w/v) DTPA, respectively. Therefore, several working solutions of AHNA were prepared containing 0.01–0.9% (w/v) sulfite and 0.001–0.09% (w/v) DTPA, taking into account that 900 μL AHNA will be used in a final volume of 3000 μL of the reacting mixture. The changes in the absorbance of these solutions as a function of time were taken as measures of their stability. It was found that working solutions of AHNA containing $\geqslant 0.1\%$ (w/v) sulfite and $\geqslant 0.01\%$ (w/v) DTPA were so stable that their absorbances remained almost constant for at least 48 h of preparation. Thus to provide a stable AHNA solution and confer enhanced selectivity for the proposed method, the working solution of AHNA was prepared as containing 0.3% (w/v) sulfite and 0.06% (w/v).

3.2. Effect of acetate concentration

The absorbance of uncatalyzed reaction (A_u) and absorbance of catalyzed reaction (A_c) by 2.0 ng mL^{-1} Mo^{6+} was increased with the increase of acetate concentration with the variation of 6.0–30.0 mmol L^{-1}. However, the sensitivity ($A_c - A_u$) had a maximum value in the 27 mmol L^{-1} acetate concentration (Fig. 2a); therefore in the subsequent study the concentration of acetate was fixed 27 mmol L^{-1}.

3.3. Effect of AHNA concentration

The A_c, A_u and $A_c - A_u$ values increased almost linearly with AHNA concentration in the range 2.0–11.0 mmol L^{-1} (Fig. 2b). However, in order to provide high sensitivity and a moderate reagent blank, an AHNA concentration of 9.0 mmol L^{-1} was adopted in the recommended procedure.

3.4. Effect of H_2O_2 concentration

The A_c, A_u and $A_c - A_u$ values were sharply increased with H_2O_2 concentration up to 20 mmol L^{-1}. However, they were almost independent of H_2O_2 concentration in the range 10–62.5 mmol L^{-1} (Fig. 2c). Therefore, a H_2O_2 concentration of 35 mmol L^{-1} was adopted in the recommended procedure.

3.5. Calibration and sensitivity

Under the optimized conditions, calibration curves were constructed for the determination of Mo(VI) according to the recommended procedure in Section 2.4. The linearity was maintained between 0.1 and 4.0 ng mL^{-1} with a correlation coefficient of 0.9986 ($A = 0.281C + 0.608$). The detection limit was 0.04 ng mL^{-1} ($3\sigma_{bl}/m$, $n = 15$).

3.6. Analysis of Mo(VI) in water samples

In order to test the utility and reliability of the proposed method, different water and waste water samples were analyzed. The results are shown in Table 1. In all cases the spiked recoveries confirmed the reliability of the proposed method.

4. Conclusion

In this study a simple, sensitive and low-cost spectrophotometric procedure for the determination of molybdenum ion in water and waste water sample was proposed. The method did not require any separation or preconcentration steps and was applied directly to the determination of trace levels of Mo(VI) in water and waste water samples. The high sensitivity of the proposed method makes more advantages favorable for Mo(VI) determination compared with the costly methods.

References

Burguera, J.L., Burguera, M., Rondon, C., 2002. Talanta 58, 1167–1175.

Carrion, N., Llanos, A., Benzo, Z., Fraile, R., 1986. At. Spectrosc. 7, 52–55.

Danko, B., Dybczynski, R., 1997. J. Radioanal. Nucl. Chem. 216, 51–57.

Ferreira, S.L.C., Dos-Santos, H.C., Campos, R.C., 2003. Talanta 61, 789–795.

Greenberg, E., Clesceri, L.S., Eaton, A.D. (Eds.), 2000. Standard Methods for the Examination of Water and Wastewater. American Public Health Association, Washington, DC.

Jonnalagadda, S.B., Dumba, M., 1993. Fresenius J. Anal. Chem. 345, 673–678.

Mousavi, M.F., Karami, A.R., 2000. Microchem. J. 64, 33–39.

Mubarak, A.T., Mohamed, A.A., Fawy, K.F., Al-Shihry, A.S., 2007. Talanta 71, 632–638.

Puri, S., Dubey, R.K., Gubta, M.K., Puri, B.K., 1998. Talanta 46, 655–664.

Pyrzynska, K., 2007. Anal. Chim. Acta 590, 40–48.

Reid, H.J., Bashammakh, A.A., Goodal, P.S., Landon, M.R., Connor, C., Sharp, B.L., 2008. Talanta 75, 189–197.

Resende-Boaventura, G., Da-Rocha-Hirson, J., Erthal-Santelli, R., 1994. Fresenius J. Anal. Chem. 350, 651–652.

Rezaei, B., Majidi, N., 2007. Spectrochim. Acta A: Mol. Biomol. Spectrosc. 66, 869–873.

Shrives, K., Agrawal, K., Harmukh, N., 2009. J. Hazard. Mater. 161, 325–329.

Soylak, M., Sahin, U., Elci, L., 1996. Anal. Chim. Acta 322, 111–115.

Soylak, M., Elci, L., Dogan, M., 1997. Kuwait J. Sci. Eng. 24, 87–92.

Sun, Y.C., Yang, N.Y., Tzeng, S.R., 1999. Analyst 124, 421–424.

Tyszczuk, K., Korolczuk, M., 2008. Anal. Chim. Acta 624, 232–237.

Xiong, Y., Zhou, Z.R., Wu, F.H., 2007. J China Univ. Min. Technol. 17, 418–423.

Yatsimirskii, K.B., Afanasva, L.P., 1956. Zh. Anal. Khim. 11, 319–323.

Zarei, K., Atabati, M., Ilkhani, H., 2006. Talanta 69, 816–821.