Available online at www.joac.info

ISSN: 2278-1862

Journal of Applicable Chemistry

2014, 3 (3): 1165-1170

(International Peer Reviewed Journal)

Sequential Spectrophotometric Determination of Trace Amounts of Periodate (IO_4^-) and Molybdate (MoO_4^{2-}) in Synthetic Mixtures and Water Samples

Pooja V. Jagasia*and Harshada R. Desai

*Department of Chemistry, B.N. Bandodkar College of Science, University of Mumbai,
Thane-400601., Maharashtra, **INDIA**

Email: jagasiapooja10@gmail.com

Accepted on 11th April 2014

ABSTRACT

A sensitive and specific spectrophotometric method has been developed for the simultaneous determination of periodate and molybdate at trace levels. The method is based on the colored product of the reaction of periodate with iodide in acidic medium and its determination spectrophotometrically at 358 nm in presence of molybdate. The molybdate analysis method is based on formation of unextractable colored complexes of it with tannic acid .Different variables affecting the reactions are optimised. The method is precise and accurate and has been applied to synthetic mixtures and water samples.

Keywords: Periodate, Molybdate,Tannic acid, water samples, Spectrophotometric estimation.

INTRODUCTION

Periodate (IO_4^-) and molybdate (MoO_4^{2-}) are important oxidants [1, 2] which can oxidise a number of compounds. They have been used for the oxidation of many organic substrates. Periodate and molybdate have been reported to play an important role in biochemical studies [3, 4]. They form an integral part of many biological and biochemical reactions which take place in plants as well as animals.

The periodate anion (IO_4^-) attacks vicinal diols to cleave the carbon-carbon bond by oxidation reaction, leading to the formation of aldehydes. The relative quantities of periodate consumed in this process or aldehydes produced can be useful in determining the structure of organic compounds, especially polysaccharides. Periodate oxidation has been widely used as a routine method for elucidation of structures in carbohydrates [5], quantitative determination of sugars in polysaccharides [6] and oxidation of organic [7] as well as inorganic ions [8]. Periodate ion also exhibits anti-carcinogenic activity due to its role as an oxidising agent. In vitro treatment of human peripheral blood lymphocytes (a form of white blood cells) with periodate has increased their cytotoxicity against leukaemia cells [9]. Periodate anion in the form of periodic acid in Periodic acid–Schiff's (PAS) stain is commonly used to assist in the diagnosis of several medical conditions including different types of cancers [10] like leukaemia [11].
Molybdate (MoO_4^{2-}) is an essential trace ion for plants and animals and a vital factor in nutrition for several enzymes to function correctly. These enzymes include aldehyde oxidase, sulphite oxidase and xanthine oxidase [12]. It is an essential component of several multimineral supplements. Anti-diabetic

properties of molybdate compounds have also been reported [13]. Combination of molybdate with the medicinal plant *Teucrium polium L*. can improve islet cells function before their transplantation. It results in greater insulin secretion which can be used in the therapy for diabetes [14]. Deficit of molybdate anion may contribute to abnormalities of iron metabolism and its utilization [12]. Molybdate helps the body detoxify sulphites, which can induce shortness of breath, respiratory arrest etc. It functions as a cofactor for the enzyme sulphite oxidase which assists in breaking down sulphite build-up in the body by transforming sulphites into harmless sulphates [15].

A number of spectrophotometric methods for the determination of periodate have been described in the literature. Periodate anion has been determined spectrophotometrically based on its reaction with methylene green in the presence of iodide [16], benzhydrazide [17], salicyl aldehyde guanylhydrazone [18] among others. Spectrophotometric determination of molybdate has been extensively studied by employing reagents such as xylenol orange [19], phenylfluorone [20], thiolactic acid [21], thiocynate using thioglycollic acid as a reductant [22] among others. Until now, no method has been developed for the sequential spectrophotometric determination of periodate (IO_4^-) and molybdate (MoO_4^{2-}). In this paper an attempt has been made to develop a simple, rapid, sensitive, fast and cost effective method for the sequential spectrophotometric determination of periodate (IO_4^-) and molybdate (MoO_4^{2-}) that would be useful in routine water quality laboratory.

MATERIALS AND METHODS

Apparatus: All glassware used for the experimental purpose were made up of Pyrex or Borosil glass. The burette, pipette and standard flasks were calibrated by the method described by Vogel [23]. The absorption measurements were carried out on a spectrophotometer, model EQ-822, supplied by Equiptronics, Powai using 1-cm matched glass cells. The spectrophotometer was calibrated by measuring the absorption spectra of potassium chromate in potassium hydroxide solution and that of potassium permanganate in sulphuric acid solution [24]. A digital pH meter model EQ-610, supplied by Equiptronics, Powai having an accuracy of ±0.02 pH and resolution of 0.01 pH was used to measure the pH of the solutions. The pH meter was calibrated with standard buffer solutions of pH 7.0, 4.0 and 9.2. A single pan digital analytical balance of series CA-223, supplied by Contech, having sensitivity of 0.001 g was used for weighing chemicals, reagents and samples.

Reagents: All the chemicals used were of A.R. grade. Distilled water was used for preparing standard solutions as well as for all experimental work.

Preparation of experimental solutions: The stock solution of periodate (1000 µg / mL) was prepared by dissolving 0.3013 g of potassium periodate [KIO_3] in distilled water in the presence of concentrated sulphuric acid. The resulting clear solution was diluted to 250 cm^3 with distilled water in a standard volumetric flask. This stock solution was standardized titrimetrically by the procedure mentioned in the literature [25]. Appropriate dilution of stock solution was carried out to obtain solutions of desired concentration of periodate. The stock solution of molybdate (1000 µg / mL) was prepared by first dissolving 1.932 g of ammonium molybdate [$(NH_4)_6\ Mo_7O_{24}.\ 4H_2O$] in distilled water. Slight turbidity develops. To this solution, liquor ammonia was added dropwise with constant stirring, till a clear solution was obtained. This clear solution was diluted to 250 cm^3 in a standard volumetric flask. The stock solution was standardized gravimetrically using oxime solution [26]. Appropriate dilution of the stock solution was carried out to obtain solutions of desired concentration of molybdate. A 0.15 M iodide solution was prepared by dissolving 1.245 g of potassium iodide (KI) in distilled water and diluting it to 50 cm^3 in a standard volumetric flask.

Tannic acid solution (1%) was prepared by dissolving weighed amount in distilled water and then diluting it up to the mark. Citrate buffer solution (0.1 M) of pH 6 was prepared by first preparing citric acid (0.1 M) and sodium citrate (0.1 M) solutions. 2.101 g of citric acid was dissolved in distilled water and diluted to

100 cm^3 in a standard volumetric flask. Sodium citrate solution was prepared by dissolving 2.941 g in distilled water and diluting it to 100 cm^3 in a standard volumetric flask. 9.5 cm^3 of 0.1 M citric acid solution and 40.5 cm^3 of 0.1 M sodium citrate solution were transferred into a 100 cm^3 standard volumetric flask and diluted upto the mark. Solution of nitrate (5000 µg) was prepared by dissolving 0.685 g of sodium nitrate ($NaNO_3$) in distilled water and diluting it to 100 cm^3 with distilled water in a standard volumetric flask.Solution of borax (10,000 µg / mL) was prepared by dissolving 1.137 g of borax ($Na_2B_4O_7$. $10H_2O$) in distilled water and diluting it to 100 cm^3 with distilled water in a standard volumetric flask. The solutions of various foreign ions were prepared by dissolving their A.R. grade salts in distilled water or dilute acids as required. The solutions of various anions were prepared by dissolving their A.R. grade sodium, potassium or ammonium salts in distilled water.

Reference Method: To a series of 10 cm^3 standard volumetric flasks containing 1-6 µg of standard periodate solution, 2 cm^3 of citrate buffer solution of pH 6 and 1 cm^3 of 0.15 M iodide solution were added. The solution was diluted upto the mark with distilled water and the absorbance for periodate was taken at 352 nm, during first three minutes after initiation of the reaction as per the procedure mentioned in the literature [27].

Proposed method: To a series of 10 cm^3 standard volumetric flasks containing 0.2-5 µg of standard molybdate solution, 1 cm^3 of 1% tannic acid solution was added. The pH of the solution was between 6.5-7.5. It was diluted upto the mark with distilled water and the absorbance for molybdate was measured at 435 nm in accordance with the procedure given in the literature [28].

Sequential spectrophotometric determination of periodate and molybdate in a mixture: An aliquot of solution containing 1-6 µg of periodate (IO_4^-) and 0.2-5 µg of molybdate (MoO_4^{2-}) was transferred into a 10 cm^3 standard volumetric flask and molybdate was masked by the addition of 1 cm^3 nitrate solution (5000 µg). The absorbance for periodate was measured by following the reference method. The resulting solution was transferred to a 20 cm^3 standard volumetric flask. Demasking of molybdate was carried out by the addition of 0.4 cm^3 borax solution (10,000 µg / mL). The absorbance for molybdate was measured by following the proposed procedure.

Effect of foreign ions: The effect of foreign ions on the sequential spectrophotometric determination of periodate and molybdate was studied by adding a definite amount of the desired foreign ions to 5 µg of periodate and 5 µg of molybdate and treating the mixture as per the developed procedure. The tolerance limit was taken as the amount of ion causing an error of not more than ±2 % in the absorbance values.

Sequential spectrophotometric determination of periodate and molybdate in synthetic mixtures: A number of synthetic mixtures containing periodates, molybdates and other commonly associated anions were prepared and treated as per the developed procedure. The treatment was carried out covering concentrations within the dynamic ranges of the species, using different concentrations of these anions.

Sequential spectrophotometric determination of periodate and molybdate in environmental water samples: Water samples were collected from Koparkhairane lake in Koparkhairane city, India and Thane creek near B.N.Bandodkar College of Science, Thane, India. Each 50 cm^3 filtered environmental water sample was boiled and reduced to 20 cm^3. It was treated with 0.5-1 cm^3 of conc. HNO_3, neutralised with dilute ammonia and again heated for 5 minutes. The resulting solution was cooled, filtered with Whatman filter paper no. 41 and diluted to 25 cm^3 with distilled water in a standard volumetric flask. An aliquot of each sample was analysed for periodate and molybdate. They tested negative. To appropriate aliquots of these samples, known amounts of IO_4^- and MoO_4^{2-} were added and then analysed by the proposed procedure.

RESULTS AND DISCUSSION

Calibration graph: The adherence to Beer's law was studied by measuring the absorbance value of the series of solutions containing different concentrations of MoO_4^{2-}. A linear calibration graph drawn between absorbance and molybdate concentration indicates that MoO_4^{2-} may be determined in the range 0.2-5.0 µg cm-1 cm^{-3} (Fig. 1). This range was also confirmed from Ringbom's plot.

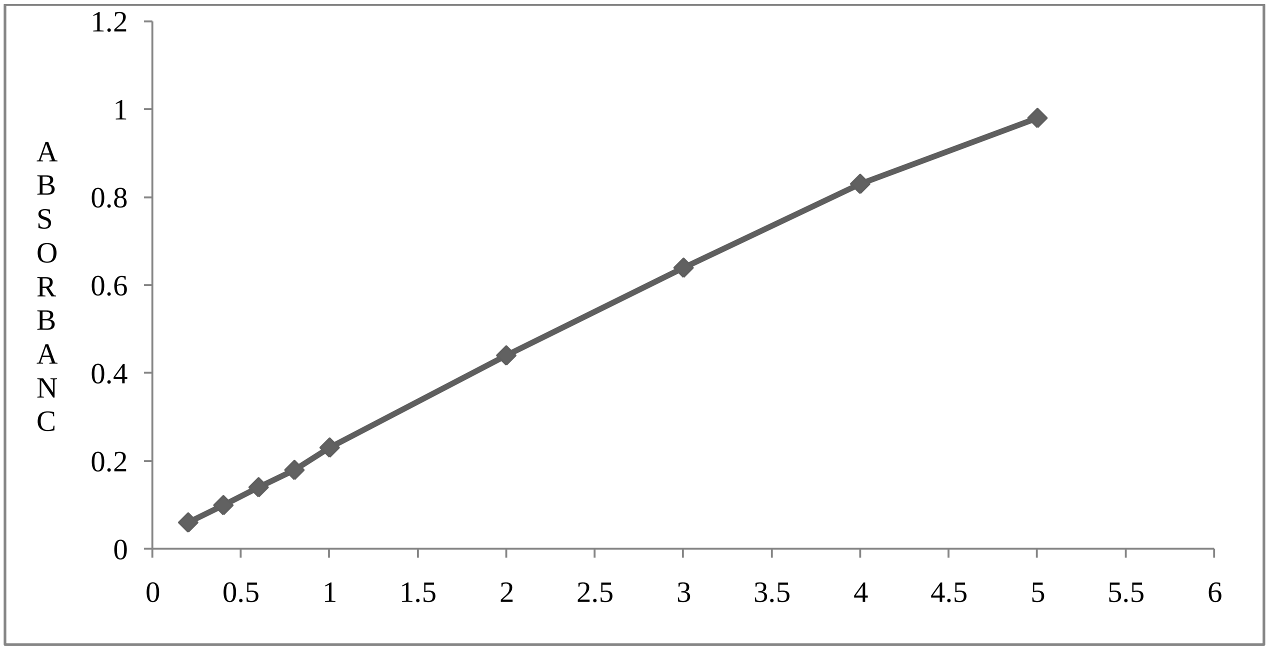

Fig. 1: Calibration curve for molybdate (MoO_4^{2-}) using Tannic acid as a reagent.

Effect of foreign ions: In order to assess the possible applications of the proposed method, the effect of foreign ions on 5 µg of periodate and 5 µg of molybdate was studied. The tolerance limit was considered to be the amount that caused a ±2 % deviation in the absorbance value. The results are summarized in table 1. The results reveal that various foreign ions can be tolerated at satisfactory levels.

Table 1: Effect of foreign ions on the determination of periodate (5 µg / mL) and molybdate (5 µg / mL)

Foreign ions	**Tolerance limit (µg / mL)**	
	Periodate (5 µg / mL)	**Molybdate (5 µg / mL)**
$C_2O_4^{2-}$	1000	1000
WO_4^{2-}	1000	500
SO_4^{2-}	2000	1000
SO_3^{2-}	2000	1000
$S_2O_3^{2-}$	1000	500
SCN^-	2000	1000
IO_3^-	2000	1000
NO_2^-	10,000	1000
EDTA	500	250
I^-	2000	1000
CH_3COO^-	2000	1000

APPLICATIONS

The proposed method under the already established optimum conditions was satisfactorily applied for the determination of IO_4^- and MoO_4^{2-} in synthetic mixtures and environmental water samples. The results are highly reproducible and are given in tables 2 and 3. The recoveries for the different added concentrations of IO_4^- and MoO_4^{2-} are in the range of 93-105%. The results show that the proposed method is suitable for determination of trace amounts of IO_4^- and MoO_4^{2-} in synthetic mixtures and environmental water samples.

Table 2: Determination of IO_4^- and MoO_4^{2-} in synthetic mixtures

Synthetic mixture			**Reference Method (IO_4^-)**		**Proposed Method (MoO_4^{2-})**	
	IO_4^- added (µg cm-1)	**MoO_4^{2-} added (µg cm-1)**	**[a]IO_4^- found (µg cm-1 cm^{-1})**	**% Recovery**	**[a]MoO_4^{2-} found (µg cm-1 cm^{-1})**	**% Recovery**
[b]1.	4	3.5	4.1± 0.058	102.5	3.47± 0.057	99.14
[c]2.	2	3	2.1± 0.058	105	2.97± 0.057	99
[d]3.	6	2.5	5.9± 0.12	98.33	2.43± 0.11	97.2

a- Mean± standard deviation (n=3),
b- IO_4^- (4 µg / mL) + MoO_4^{2-} (3.5 µg / mL) + $C_2O_4^{2-}$ (5 µg / mL) + SO_3^{2-} (10 µg / mL)
c- IO_4^- (2 µg / mL) + MoO_4^{2-} (3 µg / mL) + WO_4^{2-} (5 µg / mL) + SCN^- (10 µg / mL)
d- IO_4^- (6 µg / mL) + MoO_4^{2-} (2.5 µg / mL) + I^- (5 µg / mL) + SO_4^{2-} (6 µg / mL)
e-

Table 3: Determination of IO_4^- and MoO_4^{2-} in environmental water samples

[b]Water sample			**Reference Method (IO_4^-)**		**Proposed Method (MoO_4^{2-})**	
	IO_4^- added (µg cm-1)	**MoO_4^{2-} added (µg cm-1)**	**[a]IO_4^- found (µg cm-1 cm^{-1})**	**% Recovery**	**[a]MoO_4^{2-} found (µg cm-1 cm^{-1})**	**% Recovery**
[c]1.	4	1	4.1± 0.058	102.50	0.93± 0.029	93
[d]2.	2	2	2.1± 0.058	105	1.83± 0.058	91.50

a- Mean± standard deviation (n=3)
b- Gave no test for periodate(IO_4^{2-}) and molybdate(MoO_4^{2-})
c- Koparkhairane lake water sample
d- Thane creek water sample

CONCLUSIONS

This method describes a simple, rapid, sensitive spectrophotometric procedure for the sequential determination of periodate and molybdate in water samples. It provides a good reproducibility and lower limit of detection. The proposed method has the advantage of enabling a wide range of determination without the need for extraction or heating, which is often a prerequisite in sequential separation. When compared to other techniques which require preconcentration process and separation prior to analysis, the present method is not time consuming and gives accurate results. The results of this study clearly show the potential and versatility of this method, which could be applied to monitoring of periodate and molybdate spectrophotometrically in water samples. Although many sophisticated and high cost instrumental techniques like ICP-MS, AAS, etc. are available for the determination of anions at trace levels, the factors such as low cost of the instrument, ease of handling, lack of need for consumables, and almost no maintenance have caused spectrophotometry to remain a popular and inevitable technique, particularly in the laboratories of developing countries with a limited budget.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the Principal, Dr. (Mrs.) M.K. Pejaver, B. N. Bandodkar College of Science for providing the necessary facilities to carry out the present work.

REFERENCES

[1] M.Gaikwad, D. Silva, Pérez-Bendito, *Analyst*, **1994**, 119, 1819-1824.
[2] P.R.S. Ribeiro, L. Pezza, H.R. Pezza, *Eclet. Quím*. **2010**, 35, 3.
[3] M. Kobayashi, E. Ichishima, *J. Carbohydr. Chem*. **1991**, 10, 4, 635-644.
[4] R.J.P. Williams, J.J.R. Fraústo da Silva, *Biochem. Biophys. Res. Commun*. **2002**, 292, 2, 293–299.
[5] J.K. Hamilton, F. Smith, *J. Am. Chem. Soc.* **1956**, 78, 22, 5910–5912.
[6] O.P. Bahl, T.L. Hullar, F. Smith, *J. Org. Chem.* **1964**, 29, 5, 1076–1078.
[7] T.G. Halsall, E.L. Hirst, J.K.N. Jones, ***J. Chem. Soc.*** **1947**, 172, 1427-1432.
[8] S.C. Hiremath, S.M. Tuwar, S.T. Nandibewoor, *Indian Journal of Chemistry*, **1999**, 38 A, 61-64.
[9] I. Noda, S. Fujieda, H. Saito, T. Saito, T. Otsubo, M. Yagita, *Int. J. Immunopharmacol*. **1998**, 20, 1-3, 15-27
[10] A.F. Lee, H. Rees, D.A. Owen, D.G. Huntsman, *Am. J. Surg. Pathol*. **2010**, 34, 7, 1007-13.
[11] S.K. Pattari, N. Varma, G. Garewal, *Internet J. Hematol.* **2003**, 1, 1.
[12] M.S. Seelig, *Am. J. Clin. Nutr*. **1972**, 25, 10, 1022-1037.
[13] A. Levina, A.I. McLeod, J. Seuring, P.A. Lay, *J. Inorg. Biochem.* **2007**, 101, 11-12, 1586-1593.
[14] S.S. Mohseni Salehi Monfared, S. Pournourmohammadi, *Biol. Trace. Elem. Res.* **2010**, 133, 2, 236-241.
[15] R. Papaioannou, C.C. Pfeiffer, J. Orthomol. *Psychiatry*, **1984**, 13, 105.
[16] G. Bagherian, M.A. Chamjangali, N. Goudarzi, N. Namazi, *Spectrochimica Acta Part A*, **2010**, 76, 29-32.
[17] A.M. Escarrilla, P.F. Maloney, P.M. Maloney, *Anal. Chim. Acta.* **1969**, 45, 1, 199-201.
[18] J.J.B. Nevado, P.V. Gonzàlez, *Analyst*, **1989**, 114, 243-244.
[19] A. Majeed, J. Iqbal, S. Kausar, *Jour. Chem. Soc. Pak.* **1991**, 13, 3, 209-212.
[20] M.F. El-Shahat, M.Z. Mostafa, M. Monshi, *Microchem. J.* **1985**, 31, 1, 56-60.
[21] J.S. Fritz, D.R. Beuerman, *Talanta*, **1972**, 19, 3, 366-369.
[22] S.A. Mir, A.A. Ahangar, A.S. Bhat, *Int. J. ChemTech. Res.* **2012**, 4, 2, 565-571.
[23] G.H. Jeffery, J. Bassett, J. Mendham, R.C. Denney, A.I. Vogel's Text Book of Quantitative Inorganic Analysis including Elementary Instrumental Analysis, ELBS and Longman, New York, **1978**, 4th ed., 47-82.
[24] E.B. Sandell, Colorimetric Determination of Traces of metals, Interscience Publishers, New York, **1965**, 3rd ed.
[25] *J.D. McSweeny, R.M. Rowell, G.C. Chen, T.L. Eberhardt, S. Min, BioResources,* ***2008****, 3, 1, 204-216.*
[26] G.H. Jeffery, J. Bassett, J. Mendham, R.C. Denney, A.I. Vogel's Text Book of Quantitative Inorganic Analysis including Elementary Instrumental Analysis, ELBS and Longman, New York, **1978**, 4th ed., 472.
[27] A. Afkhami, T. Madrakian, A.R. Zarei, *Anal. Sci*. **2001**, 17, 10, 1199-202
[28] P.V. Jagasia, H.R. Desai, *Am. J. PharmTech Res.* **2013**, 3, 2, 603-615.