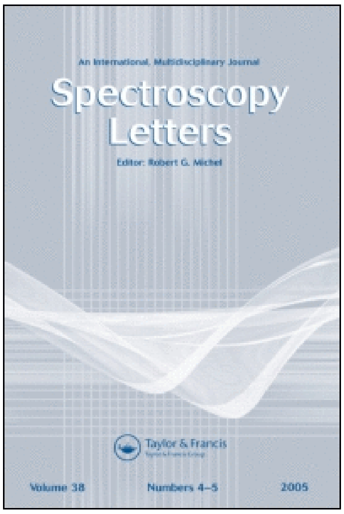

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

ON THE INTERACTION BETWEEN AZIDE AND MANGANESE IONS AT SEVERAL OXIDATION STATES

Horacio D. Moya[a]; Edwardo A. Neves[b]; Nina Coichev[a]
[a] Instituto de Química, Universidade de São Paulo, São Paulo, SP-Brazil [b] Departamento de Química, Universidade Federal de São Carlos, São Carlos, SP-Brazil

To cite this Article Moya, Horacio D. , Neves, Edwardo A. and Coichev, Nina(2001) 'ON THE INTERACTION BETWEEN AZIDE AND MANGANESE IONS AT SEVERAL OXIDATION STATES', Spectroscopy Letters, 34: 5, 537 — 547
To link to this Article: DOI: 10.1081/SL-100106869
URL: http://dx.doi.org/10.1081/SL-100106869

SPECTROSCOPY LETTERS, 34(5), 537–547 (2001)

ON THE INTERACTION BETWEEN AZIDE AND MANGANESE IONS AT SEVERAL OXIDATION STATES

Horacio D. Moya,[1] **Edwardo A. Neves,**[2] **and Nina Coichev**[1,*]

[1]Instituto de Química, Universidade de São Paulo,
C. P. 26.077, CEP 05599-970 São Paulo, SP-Brazil
[2]Departamento de Química, Universidade Federal de
São Carlos, C. P. 676 CEP 13.565-905 São Carlos,
SP-Brazil

ABSTRACT

The interaction between azide and manganese ions, at several oxidation states (II, III, IV, V, VI and VII), has been investigated in aqueous medium at 25.0 ± 0.1 °C and ionic strength $2.0\,\mathrm{mol} \cdot \mathrm{L}^{-1}(\mathrm{NaClO_4})$. Spectral data were obtained from absorbance measurements in order to calculate the molar absorptivity. The molar absorptivity values calculated, at 430 nm, for $[\mathrm{Mn(N_3)_3}]$, $[\mathrm{Mn(N_3)_4}]^-$ and $[\mathrm{Mn(N_3)_5}]^{-2}$ were 230, 3,700 and 6,600 $\mathrm{mol^{-1} \cdot L \cdot cm^{-1}}$, respectively. Mn(IV) and Mn(V) are not stable in azide aqueous solution medium and spectral characteristics are similar to $\mathrm{Mn(III)/N_3^-}$ complexes. Additions of permanganate or manganese(VI) solution, as K_2MnO_4, to several azide buffers solutions,

---

*Corresponding author. E-mail: ncoichev@quim.iq.usp.br

N_{3-}/HN_3, have produced species which have shown similar spectral characteristics with $\bar{\boldsymbol{\varepsilon}} \cong 10^4\,\mathrm{mol^{-1} \cdot L \cdot cm^{-1}}$ at 438 nm.

Key Words: Azide; Manganese; Spectrophotometric studies

INTRODUCTION

It has been shown that azide medium, $[N_3^-] = 0.5\,\mathrm{mol \cdot L^{-1}}(\mathrm{pH} = 5.5)$ is an optimal experimental condition, representing a sensitive analytical method, for the determination of S(IV) in environmental samples as the hydrolysis product of SF_6[1]. This reaction was based on the Co(II) induced autoxidation, as formerly studied by P. Senise[2], since the concentration of Co(III) azide complex formed is a linear relationship with the initial S(IV) concentration. As the molar absorptivity of Co(III) at 365 nm is high ($\bar{\boldsymbol{\varepsilon}} \cong 22,000\,\mathrm{mol^{-1} L \cdot cm^{-1}}$), it is possible to determine S(IV) in the range of 10^{-6} to $10^{-4}\,\mathrm{mol \cdot L^{-1}}$.

The synergistic effect of the Mn(II) ions on the S(IV) induced autoxidation of metal ions, accelerates the entire process, such that Mn(II) becomes essential in the working solution[3]. This synergistic effect has been the object of other studies involving the autoxidation of metal ions, such as Fe(II)[4] and Co(II)[5], with an interpretative study where free radical formation takes an important role in the process[4,5].

This paper deals with the interaction between manganese with azide ions in aqueous solution in order to obtain some additional information about spectrophotometric characteristics of the manganese ion at several oxidation states in azide medium.

EXPERIMENTAL

Reagents

All reagents were from AR or CP specification from Merck or Fluka Chemie A. G. Sodium perchlorate solution ($5.00\,\mathrm{mol \cdot L^{-1}}$) utilized to make up the ionic strength of working solutions, was standardized by taking small volume of the solution and drying in an oven at 120 °C until constant weight.

Manganese(II) perchlorate solution ($1.80\,\mathrm{mol \cdot L^{-1}}$) was prepared from the direct reaction of excess carbonate with $6\,\mathrm{mol \cdot L^{-1}}$ perchloric acid for 2 days, constantly stirring at room temperature. After filtering, free perchloric acid was used to adjust pH to 5.5, in order to avoid hydrolysis. Standardization was carried out by complexometric titration with EDTA[6].

Sodium azide solution ($4.80\,\mathrm{mol}\cdot\mathrm{L}^{-1}$) was prepared directly from the salt. Standardization was carried out by adding a known volume of standard sulfuric acid solution, boiling to remove volatile hydrazoic acid, HN_3, followed by back titration of the remaining strong acid with standard sodium hydroxide solution.

Standard perchloric acid solution ($2.00\,\mathrm{mol}\cdot\mathrm{L}^{-1}$) was added to the working solutions to displace hydrazoic acid from the azide ions to promote a buffer solution.

Potassium permanganate solution was prepared and standardized using the conventional method[7].

Potassium manganate(VI) solution and sodium manganate(V) salt were prepared as described in the literature[8].

Hydrogen peroxide solution ($0.01\,\mathrm{mol}\cdot\mathrm{L}^{-1}$) was prepared by dilution from concentrated reagent (30% v/v) and standardized by using $KMnO_4$ solution[7].

In order to keep such working solutions free from oxygen, all standard solutions were previously bubbled with purified nitrogen before mixing.

RESULTS AND DISCUSSION

The Mn(II)/N_3^- Complexes

Recent studies of Mn(II) in azide buffers solutions, N_3^-/HN_3, lead to four stepwise overall constants ($\beta_1 = 4.15\,M^{-1}, \beta_2 = 6.61\,M^{-2}, \beta_3 = 3.33\,M^{-3}$ and $\beta_4 = 0.63\,M^{-4}$)[9] and showed a tendency to change colour of the solution with a formation of brownish Mn(III) azide complexes, which have a maximum absorbance peak at 430 nm (Fig. 1). Spontaneous oxidation of Mn(II) to Mn(III) by dissolved oxygen or hydrazoic acid took place at azide concentrations higher than $0.5\,\mathrm{mol}\cdot\mathrm{L}^{-1}$ and it was markedly dependent on HN_3 concentration (Fig. 2).

Figure 1 shows the absorbance changes at 430 nm due to the spontaneous oxidation of Mn(II), by dissolved oxygen, in air saturated azide buffer solutions containing Mn(II). The oxidation is more effective at high azide concentration ($E^{0\prime}\mathrm{Mn(III)/Mn(II)} = 0,42\,V$ vs. SCE, in $N_3^- = 1.0\,\mathrm{mol}\cdot\mathrm{L}^{-1}$ and $HN_3 = 0.01\,\mathrm{mol}\cdot\mathrm{L}^{-1}$)[10]. In the absence of oxygen the oxidation is almost non existent under small HN_3 concentration ($5.0 \times 10^{-2}\,\mathrm{mol}\cdot\mathrm{L}^{-1}$).

Figure 2 shows that the oxidation depends on the HN_3 concentration, so hydrazoic acid or oxygen can act as oxidizing agent (Eqns. 1 and 2):

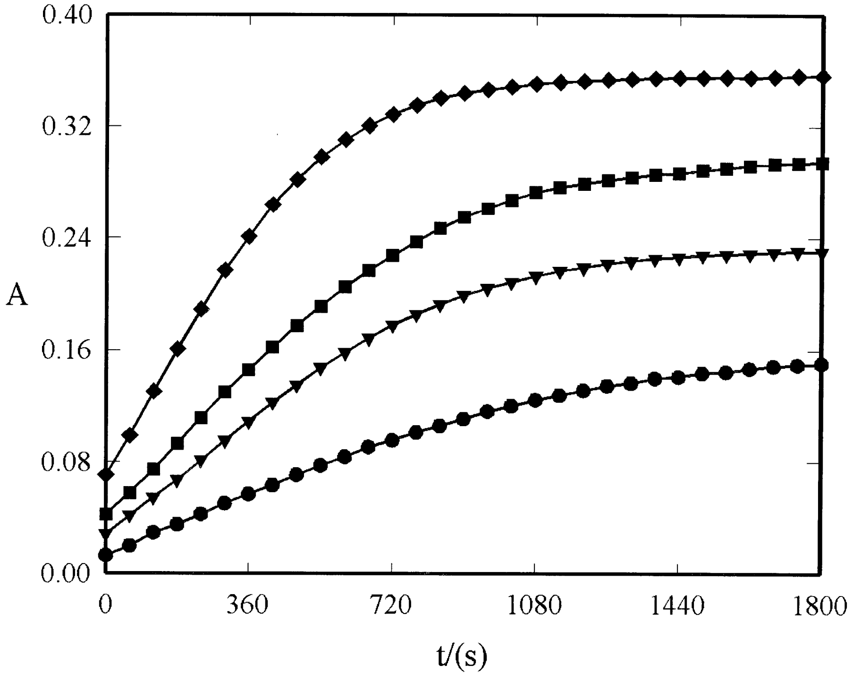

Figure 1. Absorbance changes of air saturated solutions of Mn(II)/N_{3-}. Mn(II) = $1.0 \times 10^{-1} \cdot mol \cdot L^{-1}$ and $HN_3 = 5.0 \times 10^{-2} \cdot mol \cdot L^{-1} \cdot N_{3-}$: ● = $1.0\, mol \cdot L^{-1}$, ▼ = $1.2\, mol \cdot L^{-1}$, ■ = $1.4\, mol \cdot L^{-1}$, ◆ = $1.6\, mol \cdot L^{-1}$. $\lambda = 430\, nm$, path-length = 1.00 cm.

$$2[Mn(N_3)_n]^{2-n} + 4\,HN_3 \longrightarrow 2[Mn(N_3)n]^{3-n} + N_2 + NH_4^+ + 3\,N_{3-} \quad (1)$$

$$2[Mn(N_3)_n]^{2-n} + \tfrac{1}{2}O_2 + 2HN_3 \longrightarrow 2[Mn(N_3)_n]^{3-n} + 2\,N_{3-} + H_2O \quad (2)$$

The Mn(III)/N_{3-} Complexes

The Mn(III) (10^{-6} to $10^{-4}\, mol \cdot L^{-1}$) was generated by coulometric oxidation in a solution containing a large excess of Mn(II) ($0.5\, mol \cdot L^{-1}$) in the N_{3-}/HN_3 buffer at constant ionic strength[10]. The overall formation constants for the Mn(III)/N_3^- system are: $\beta_1 = 1.2 \times 10^5\, M^{-1}$, $\beta_2 = 6.0 \times 10^8\, M^{-2}$, $\beta_3 = 2.4 \times 10^{11}\, M^{-3}$, $\beta_4 = 1.5 \times 10^{11}\, M^{-4}$ and $\beta_5 = 9.6 \times 10^{11}\, M^{-5}$. The β_1 and β_2 constants were obtained by graphic extrapolation[10].

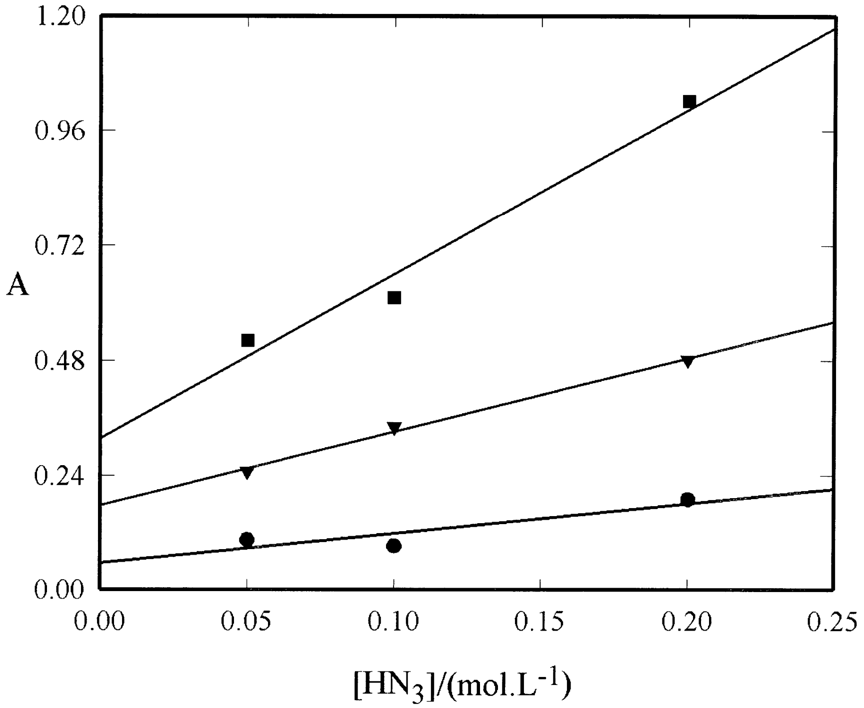

Figure 2. Absorbance changes of $1.0 \times 10^{-1}\,mol \cdot L^{-1}$ Mn(II), in several HN_3/N_{3^-} buffers solutions, Initially prepared in absence of air. N_{3^-}: ● $= 0.5\,mol \cdot L^{-1}$, ▼ $= 1.0\,mol \cdot L^{-1}$, ■ $= 1.5\,mol \cdot L^{-1}$. $\lambda = 430\,nm$, Path-length = 1.00 cm. Measurements after 50 minutes keeping the solution in contact of air without stirring.

Determination of the Molar Absorptivity for Each Species in the Mn(III)/N_3^- System

The average molar absorptivity, at the maximum absorbance peak of 430 nm, increases with azide concentration (0.44 to $3.9\,mol \cdot L^{-1}$) from 3,100 to $6,600\,mol^{-1} \cdot L \cdot cm^{-1}$, showing a stepwise complex formation[10]. Measurements in solutions containing free azide concentration lower than $0.44\,mol \cdot L^{-1}$ were not considered because the Mn(III) complexes becomes unstable and the brownish colour fades.

The average molar absorptivity, $\bar{\varepsilon}$, at 430 nm at a given free ligand concentration is:

$$\bar{\varepsilon} = \frac{A}{C_{Mn} \cdot b} \tag{3}$$

where A is the absorbance of the solution with C_{Mn}, the total concentration of Mn(III), and b is the pathlength.

The method used to calculate the molar absorptivity of each Mn(III)/N_3^- complex species is based on the equation:

$$\bar{\boldsymbol{\varepsilon}} = \frac{(\boldsymbol{\varepsilon}_0 + \beta_1 \cdot [N_3^-] \cdot \boldsymbol{\varepsilon}_1 + \beta_2 \cdot [N_3^-]^2 \cdot \boldsymbol{\varepsilon}_2 + \cdots + \beta_n \cdot [N_3^-]^n \cdot \boldsymbol{\varepsilon}_n)}{(1 + \sum_{n=1}^{n} \beta_n \cdot [N_3^-]^n)} \qquad (4)$$

And the free azide concentration can be calculated using:

$$[N_3^-] = C_{N_3^-} - [HN_3] - n_{II} \cdot [Mn(II)] - n_{III} \cdot [Mn(III)] \qquad (5)$$

where $\bar{n}$II and $\bar{n}$III are the average ligand numbers calculated with stability constants of Mn(II) and Mn(III) azide complexes, respectively[10].

Since that in the ligand range concentration studied (0.44 to $1.8\,mol \cdot L^{-1}$) only the $[Mn(N_3)_3]$, $[Mn(N_3)_4]^-$ and $[Mn(N_3)_5]^{-2}$ species are present, the average molar absorptivity at higher azide concentration ($2.0\,mol \cdot L^{-1}$) refers to the last species ($\boldsymbol{\varepsilon}_5 = 6,600\,mol^{-1} \cdot L \cdot cm^{-1}$)[10].

The equation (4) can be written as:

$$\boldsymbol{\Phi} = \frac{\bar{\boldsymbol{\varepsilon}} \cdot (1 + \sum_{n=1}^{5} \beta_n \cdot [N_3^-]^n) - \beta_5 \cdot [N_3^-]^5 \cdot \boldsymbol{\varepsilon}_5}{\beta_3 \cdot [N_3^-]^3} = \boldsymbol{\varepsilon}_3 + \frac{\beta_4 \cdot [N_3^-]}{\beta_3} \cdot \boldsymbol{\varepsilon}_4 \qquad (6)$$

From this equation, where $\varepsilon_5 = 6,600, \varepsilon_3$ and ε_4 can be calculated from the intercept and the slope of the straight line $\boldsymbol{\Phi}$ vs. $\beta_4 \cdot [N_{3^-}]/\beta_3$.

The molar absorptivity values calculated, at 430 nm, for $[Mn(N_3)_3]$, $[Mn(N_3)_4]^-$ and $[Mn(N_3)_5]^{-2}$ species were 230, 3,700 and $6,600\,mol^{-1} \cdot L \cdot cm^{-1}$, respectively.

Mn(IV) in Azide Medium

Kinetic studies performed in extremely high concentrated acid perchloric[12] and acetic[13] medium have shown that complexes manganese(IV)/N_3^- can be formed as intermediate species from the reaction between manganese(III) and HN_3.

To evaluate the possible formation and stability of Mn(IV) complexes in azide medium, spectrophotometric measurements have been made by two different ways. The first step was the preparation of Mn(IV), as $MnO(OH)_2$, freshly precipitated, by adding NaOH solution in the presence of dissolved oxygen or $NaOH/H_2O_2$ mixture, to Mn(II) $(5.10^{-4}\,mol \cdot L^{-1})$ solution. After some minutes, to allow the complete precipitation, a solution of $NaClO_4$ was carefully added drop by drop. Then a buffer solution of N_{3^-}/HN_3 (in the range $N_{3^-} = 1.0$ to $2.0\,mol \cdot L^{-1}$ and $HN_3 = 0.05$ to $1.0\,mol \cdot L^{-1}$) was added and all precipitate was completely dissolved with the solution homogenization. This procedure avoids the instantaneous mixing of the reagents because the more concentrated solution of $NaClO_4$ does not allow the direct contact of the reagents. Absorption spectra of these solutions were coincident with the one obtained for $Mn(III)/N_{3^-}$ solution. The second way was made using commercial MnO_2. When this oxide is added to the buffer the solubilization is much slower (about 2 days), and the obtained solution shows the same spectrophotometric characteristics of the $Mn(III)/N_3^-$ complexes. Thus, we could not conclude the presence of Mn(IV) in the presence of N_{3^-}/HN_3 buffer solution.

Mn(V) in Azide Medium

Mn(V) is uncommon and is only known as manganate, which is not stable in aqueous solution. When manganese(V), as a light blue salt $Na_3MnO_4 \cdot 10H_2O$[8], was added to a N_{3^-}/HN_3 buffer solution, a brownish colour appeared. The spectra of this solution is very similar to the $Mn(III)/N_{3^-}$ solution. Nevertheless, no quantitative conclusion could be achieved since the water content of the salt, $Na_3MnO_4 \cdot xH_2O$, could not be determined.

Mn(VI) and Mn(VII) in Azide Medium

The azide ion is thermodynamically unstable and is potentially a very powerful reducing agent, as inferred from the standard reduction potential of the N_2/N_{3^-} system of $-3.4\,V$[14]. In spite of that, the reactivity of the ligand toward oxidizing agents is fairly low under a variety of conditions and in the absence of a catalyst. The ligand is not oxidized by MnO_4^- or H_2O_2 in alkaline medium[15]. Hydrazoic acid, HN_3, is much more reactive and can be oxidized by strong oxidizing agents such as MnO_4^-, Ce(IV) and $Cr_2O_7^{2-}$. The stabilization of Mn(III) is possible only due to the inertia of the azide ions towards oxidation.

However, previous qualitative studies have shown that addition of $KMnO_4$ solution to a different buffer azide solution (*e.g.*, $N_{3^-} = 2.5\,mol \cdot L^{-1}$ and $HN_3 = 0.5\,mol \cdot L^{-1}$) produces evolution of nitrogen but

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

also the reduction of Mn(VII) to a species which has a high molar absorptivity value at 438 nm[16].

In the present work several quantitative experiments were carried out in order to obtain more information about this manganese ion, at higher oxidation state, which can have some analytical interest due the high molar absorptivity value at 438 nm.

Small volumes of $KMnO_4$ or K_2MnO_4 solutions were added to N_{3^-}/HN_3 buffer, at ionic strength 2.0 mol · L^{-1} kept with $NaClO_4$. The final concentration in azide ion were 0.050, 1.00 and 1.50 mol · L^{-1}, and HN_3 0.050, 0.1 and 0.2 mol · L^{-1}. The final concentrations of manganese, as $KMnO_4$ or K_2MnO_4, were 1.25×10^{-5} and 2.5×10^{-5} mol · L^{-1}. The

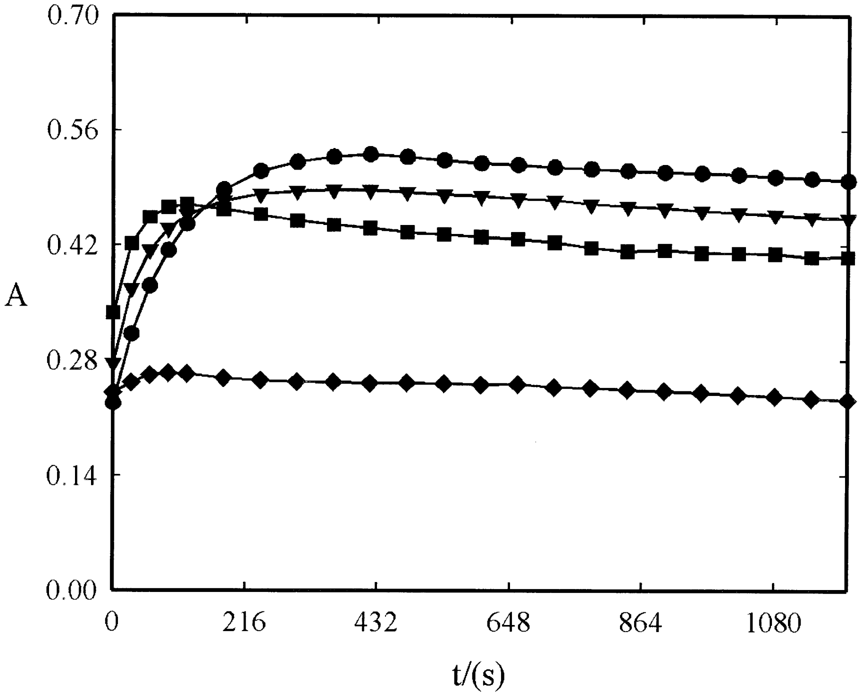

Figure 3. Absorbance changes, at 438 nm, After addition of Mn(VII) or Mn(VI) solutions in a different azide buffer. (●: $KMnO_4 = 2.5 \times 10^{-5}$ mol · L^{-1} and $HN_3 = 0.05$ mol · L^{-1}, ▼: $KMnO_4 = 2.5 \times 10^{-5}$ mol · L^{-1} and $HN_3 = 0.10$ mol · L^{-1}, ■: $KMnO_4 = 2.5 \times 10^{-5}$ mol · L^{-1} and $HN_3 = 0.20$ mol · L^{-1} and ◆: $K_2MnO_4 = 1.25 \times 10^{-5}$ mol · L^{-1} and $HN_3 = 0.1$ mol · L^{-1}. $N_{3^-} = 1.0$ mol · L^{-1} path length = 1.00 cm, reference solution: $KMnO_4 = 2.5 \times 10^{-5}$ mol · L^{-1} or $K_2MnO_4 = 1.25 \times 10^{-5}$ mol · L^{-1}, freshly prepared and in a absence of buffer).

absorption spectra (300–500 nm) presented a maximum absorption peak at 438 nm, when $KMnO_4$ or K_2MnO_4 were used.

The manganese ion complex formed, when $KMnO_4$ or K_2MnO_4 were added, was quite stable in a azide buffer solution $N_{3^-} = 1.00\,mol \cdot L^{-1}$ and $HN_3 = 0.050\,mol \cdot L^{-1}$. This manganese species formed is stable for about 10 minutes and then the absorbance value slowly decrease (Fig. 3).

The molar absorptivity calculated at 438 nm is approximately $2 \times 10^4\,mol^{-1} \cdot L \cdot cm^{-1}$ order of magnitude, which is about nine times higher than permanganate ion in aqueous solution, in a non complexing medium, and about three times higher than the $[Mn(N_3)_5]^{-2}$ species ($\varepsilon = 6,600\,mol^{-1} \cdot L \cdot cm^{-1}$).

Thus, this species formed by addition of $KMnO_4$ or K_2MnO_4 to a N_{3^-}/HN_3 buffer must be neither Mn(VII) nor Mn(III), which has much smaller molar absorptivity, at 430 nm.

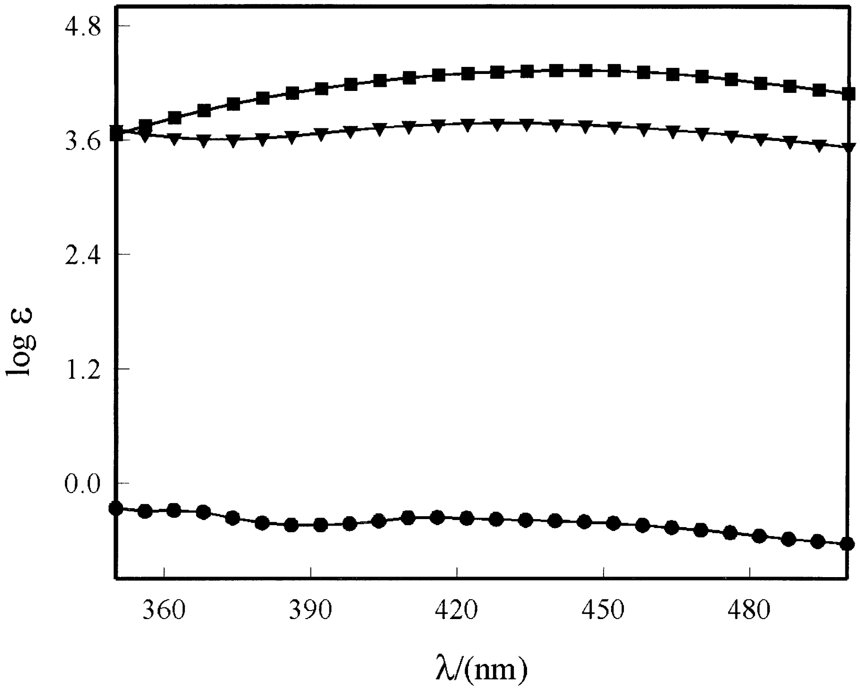

Figure 4. Logarithm of the average molar absorptivity, $\bar{\varepsilon}$, for each species of manganese ion as a function of wavelength. ● = Mn(II), ▼ = Mn(III), ■ = probably Mn(VI) obtained by addition of $KMnO_4$ or K_2MnO_4 in a azide buffer solution ($N_{3^-} = 1.0\,mol \cdot L^{-1}$ and $HN_3 = 0.10\,mol \cdot L^{-1}$).

It is interesting to note that the formation and stability in solution of this unusual manganese species depends on the concentration and Ph value of the N_{3^-}/HN_3 buffer (Fig. 3). This species formation was not observed in the absence of HN_3. At lower acidity the reaction is slower and is much faster at higher acidity ($0.20\,\mathrm{mol \cdot L^{-1}}\,HN_3$) and at N_{3^-} concentration higher than $3.0\,\mathrm{mol \cdot L^{-1}}$ as well.

The results were similar when $KMnO_4$ or K_2MnO_4 solution were employed, since the average molar absorptivity is about the same (Fig. 4).

This unusual manganese species could be Mn(VI), although MnO_2^{2+} has not been described in the literature thus far.

ACKNOWLEDGMENTS

The authors gratefully acknowledge financial support from the Brazilian Foundations (CNPq and FAPESP).

REFERENCES

1. Segundo, S.M.; Neves, E.A.; Klockow. D. The Sulfur(IV)-cobalt(II)-azide System and its Application to the Investigation of the Decomposition of Sulfur Hexafluoride under Electrical Discharges. Analyst **1994**, *119*, 1075–1076.
2. Senise, P. Spot Test for Sulfite Based on the Induced Oxidation of Cobalt-azide Solutions. Mikrochim. Acta **1957**, *5*, 640–643.
3. Gebert, J.; Neves, E.A.; Klockow. D. Evaluation of the Sulfur(IV) Catalysed Autoxidation of Cobalt(II) in an Azide Containing Medium as a Means for the Determination of Sulfite in Precipitation. Fresenius Z. Anal. Chem. **1988**, *331*, 260–267.
4. Coichev, N.; Bal Reddy, K.; Van Eldik R. The Synergistic Effect of Manganese(II) in the Sulfite-induced Autoxidation of Metal Ions and Complexes in Aqueous Solution. Atmos. Environ. **1992**, *26* (A), 2295–2300.
5. Neves, E.A.; Coichev, N.; Gebert, J.; Klockow. D. Autoxidation of Cobalt(II) in Azide Containing Medium in Presence of Sulfur(IV): An Interpretative Study. Fresenius Z. Anal. Chem. **1989**, *335*, 386–389.
6. Flaschka, H.A. *EDTA Titration*; Pergamon Press: London, 1989; 77.
7. Jeffery, G.H.; Bassett, J.; Mendham, J.; Denney, R.C. *Vogel's Textbook of Quantitative Chemical Analysis*; 5th Edition. Longmans Scientific & Technical: Avon, 1991; 370–372.

8. Brauer, G. *Química Inorgánica Preparativa*; Editorial Reverté: Barcelona, 1958; 874.
9. Moya, H.D.; Neves, E.A.; Suarez-Iha, M.E.V.; Coichev, N. Study of Complex Formation in the Manganese(II)/azide system. Talanta **1996**, *43*, 67–72.
10. Moya, H.D.; Neves, E.A.; Coichev, N. The Stabilization of Manganese(III) by Azide Ions in Aqueous Solution. Talanta **1997**, *44*, 797–803.
11. Velloso, N.C.F.; Neves, E.F.A.; Gutz, I.G.R. Spectrophotometric and Potentiometric Study of the Cobalt(II)-thiocyanate System in Aqueous Medium. Polyhedron **1985**, *4*, 2043–2050.
12. Davies, G.; Kirschenbaum, L.J.; Kustin, K. The Kinetics and Stoichiometry of the Reaction Between Manganese(III) and Hydrazoic Acid in Acid Perchlorate Solution. Inorg. Chem. **1969**, *8*, 663–669.
13. Treindl, L.; Mrákavova, M. Redox Reactions of Complex Cations in Higher Oxidation States. VII. Kinetics of the Redox Reaction of the Mn(III) Ions with Hydrazoic Acid. Chem. Zvesti **1977**, *31*, 145–152.
14. Maloy, J.T. In *Standard Potentials in Aqueous Solution*; Bard, A.J., Parsons, R., Jordan, J., Eds.; Marcell Dekker: New York, 1985; 133.
15. Neves, E.A.; Oliveira, E.; Santos, Z.L. Spectrophotometric Study of the Equilibria in Aqueous Copper(II) Azide Solutions. Talanta **1980**, *27*, 609–612.
16. Senise, P.; Neves, E.A. Data on the Complexing Power of Azide Ions with Regard to Several Metal Ions in Aqueous Solutions. An. Acad. Bras. Ciênc. **1969**, *41* (3), 333–339.

Received September 13, 2000
Accepted July 1, 2001

Downloaded At: 03:10 30 January 2011

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

Order now!

Reprints of this article can also be ordered at

http://www.dekker.com/servlet/product/DOI/101081SL100106869