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Determination of Nickel and Manganese by Kinetic H-Point Standard Addition Method

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ABSTRACT

H-point standard addition method (HPSAM) was applied to kinetic data for simultaneous determination of Ni(II) and Mn(II). The method is based on the difference between rate of complexation of 1-(2-pyridylazo)-2-naphthol (PAN) with Ni(II) and Mn(II) at pH 7.5 in Triton X-100 micellar media. Ni(II) and Mn(II) can be determined simultaneously in the concentration range 0.084-0.734 and 0.055-0.366 µg mL-1, respectively. The proposed method has successfully been applied for simultaneous determination of Ni(II) and Mn(II) in synthetic samples, spiked water samples, alloys and food products.

Key Words: *Nickel; Manganese; Kinetic; HPSAM; PAN.*

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1. INTRODUCTION

In 1988, Bosch-Reig and Campins-Falco [1, 2] presented a new technique, the H-point standard addition method (HPSAM), with which two species with overlapping spectra can be determined [3, 4]. HPSAM is based on dual-wavelength spectrophotometry and the standard addition method. HPSAM allows for the direct correction of both proportional and constant errors produced by the sample matrix. The method has also been applied to eliminate the blank [5, 6], in liquid chromatography [7], in metal speciation [8] and for the analysis of kinetic data [9-11] with time as an additional variable. For kinetic determination by applying HPSAM, the reaction of X (analyte) should be faster than that of Y (interferent). This method is based on the assumption that only X reacts with time and the analytical signal for Y does not change with time. In this case the variables to be fixed are two times t_1 and t_2. Within the time range (t_1 and t_2) absorbance of Y does not change.

The widespread role of metal ions in health and disease range from the requirement for intake of essential trace elements to toxicity associated with metal overload. Mn(II) plays an important role in a number of physiologic processes as a constituent of some enzymes and an activator of other enzymes [12]. Urease [13] as an enzyme contains nickel, and is essential for plants and some animals. But some attention has also been focussed on the toxicology of Mn(II) and Ni(II), such as the fact that excessive intake of Mn(II) can cause lesions, headache, psychotic behaviour and drowsiness [14]. Ni(II) can cause allergic reactions and certain nickel compounds are carcinogenic [15].

Several reports have been published on the simultaneous determination of Ni(II) and Mn(II) using graphite furnace atomic absorption spectrometry (GFAAS) [16], differential pulse anodic stripping voltammetry (DPASV) with a hanging mercury drop electrode (HMDE) [17] and ion chromatography [18]. All these techniques require costly instrumentation for quantitation of chemical species. Spectrophotometric methods play a prominent role, as they involve less cost and they are rapid and sensitive.

The organized molecular assemblies such as micelles are used in spectroscopic measurements due to their possible effects on the systems of interest. In the field of metal ion complex, at a concentration above critical micelle concentration (cmc) micelles form a ternary complex with advantageous properties, such as hyperchromic and bathochromic shifts, that can modify the sensitivity of the method by affecting the interferences and matrix effects [19]. The ability of micellar systems to solublize slightly soluble or even insoluble complexes has been used to enhance the analytical merit of given methods [20]. Most organic solvents that are used as extraction solvents can be classified as toxic and environmental pollutants, and some have been listed as carcinogenic by the US Environmental Protection Agency (EPA) [21]. Application of micellar systems avoids the solvent extraction step which is necessary following the formation of slightly soluble complexes in the absence of micelles.

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In the present work, kinetic-HPSAM has been developed for simultaneous determination of Ni(II) and Mn(II), using 1-(2-pyridylazo)-2-naphthol (PAN) as a chromogenic complexing reagent at pH 7.5 in Triton X-100 micellar media.

2. EXPERIMENTAL

2.1 Reagents

All reagents used were of analytical reagent grade unless otherwise stated. Double distilled water was used throughout the experiment. Stock Ni(II) and Mn(II) solutions were prepared from hydrated nickel chloride and manganese acetate respectively. Further dilutions were made as and when required. A 0.01 % solution of PAN (Merck) was prepared in dimethylformamide. A buffer solution of pH 7.5 was prepared by mixing appropriate amounts of 0.2 M borax and 0.2 M boric acid. A 1.0 % (v/v) Triton X-100 stock solution was prepared in hot distilled water.

2.2 Apparatus

Digitized UV–VIS absorption spectra were recorded using a Shimadzu 1700 spectrophotometer, with 10 mm quartz cell and measurements of pH were made with digital century pH-meter CP 901 using a combined glass electrode.

2.3 Procedure

2.3.1. Individual calibration

Appropriate volumes of Ni(II) or Mn(II) standard solutions, 2.5 mL of 1.0 % Triton X-100, 2 mL of buffer solution (pH 7.5), 1.0 mL of 0.01 % PAN solution were added into a 10 mL standard flask and volume was made up to the mark with double distilled water. A portion of the solution was transferred into a quartz cell and variations of absorbance with time were recorded at 565 nm at a time intervals of 10 s for each sample. The final concentration of Ni(II) and Mn(II) must be between 0.084-0.734 and 0.055-0.366 µg mL^{-1} respectively.

2.3.2. Kinetic-HPSAM

In a 10 mL volumetric flask, 2.5 mL of 1.0 % Triton X-100, 2 mL of buffer solution (pH 7.5), 2.0 mL of 0.01 % PAN solution (to ensure complete complexation when both Ni(II) and Mn(II) were present), appropriate amounts of Ni(II) and Mn(II) standard solutions were added and volume was made up to the mark with double distilled water. Standard additions of Ni(II) were made. The absorbance was measured at 20 and 70 s for performing kinetic-HPSAM in the proposed system.

3. RESULTS AND DISCUSSION

PAN forms colored complexes with Ni(II) and Mn(II). The complexation reaction of Mn(II) with PAN was found to be faster than that of Ni(II) in the same conditions. Figure 1 shows the absorbance time graph for the reaction of Ni(II) and Mn(II) with PAN in Triton X-100 micellar media. Reaction of Mn(II) with PAN was completed within 15 s while that of Ni(II) was not completed even after 200 s of initiation of the reaction. This difference in the kinetic behavior was used for simultaneous determination of Ni(II) and Mn(II) in the present work. The wavelength of 565 nm was selected for monitoring the kinetics of the system as both Mn(II)-PAN and Ni(II)-PAN complexes absorb at this wavelength. Figure 2 shows the overlapping absorption spectra of the PAN complexes of Ni(II) and Mn(II).

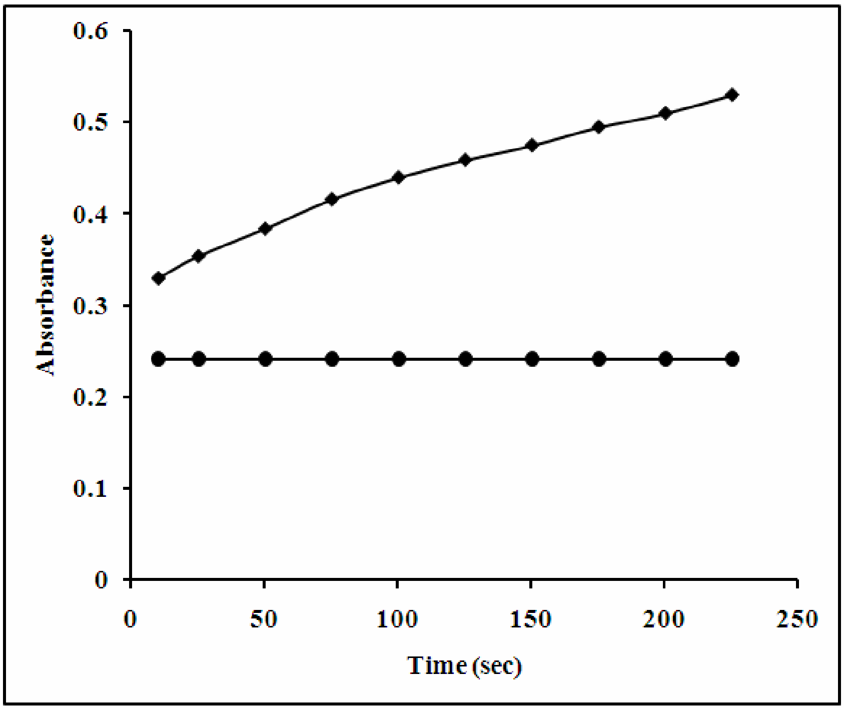


Figure 1. Absorbance-time curve for (◆) 0.294 µg mL^{-1} Ni(II) and (●) 0.183 µg mL^{-1} Mn(II). The absorbances recorded at wavelength 565 nm in fixed time (10-200 s).

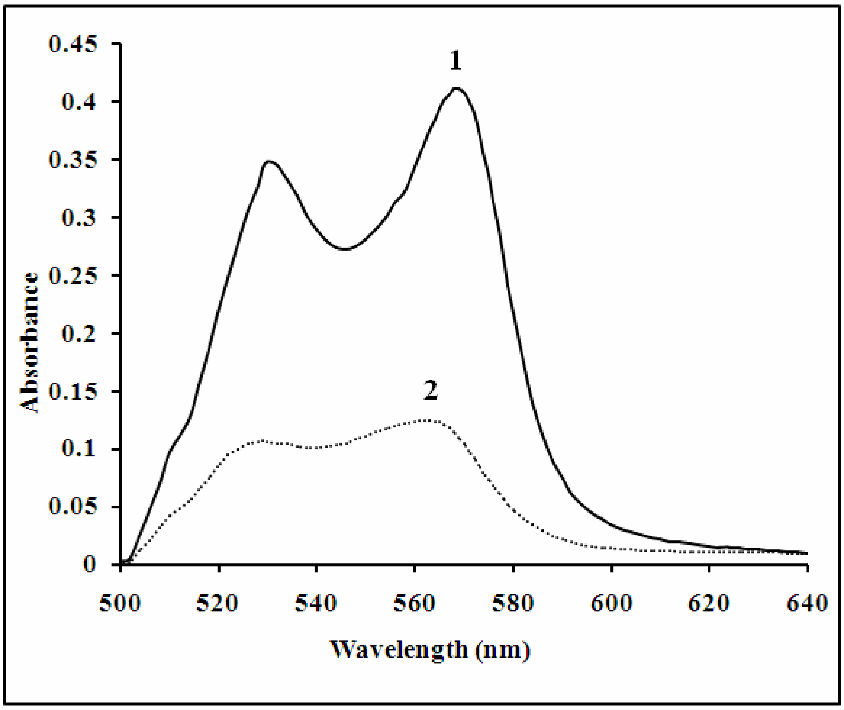


Figure 2. Absorption spectra of: (1) Ni(II)-PAN and (2) Mn(II)-PAN against blank under optimized conditions.

3.1 Optimization of Variables

The effect of pH (3.5-9.5) on the absorbance of Ni(II)-PAN and Mn(II)-PAN complexes is shown in Figure 3. For Ni(II)-PAN complex absorbance increases by increasing pH up to 7.5 and then decreased at pH>7.5. Mn(II)-PAN complex shows maximum and constant absorbance in the pH range 7.5-9.5 therefore; pH 7.5 was selected for further study.

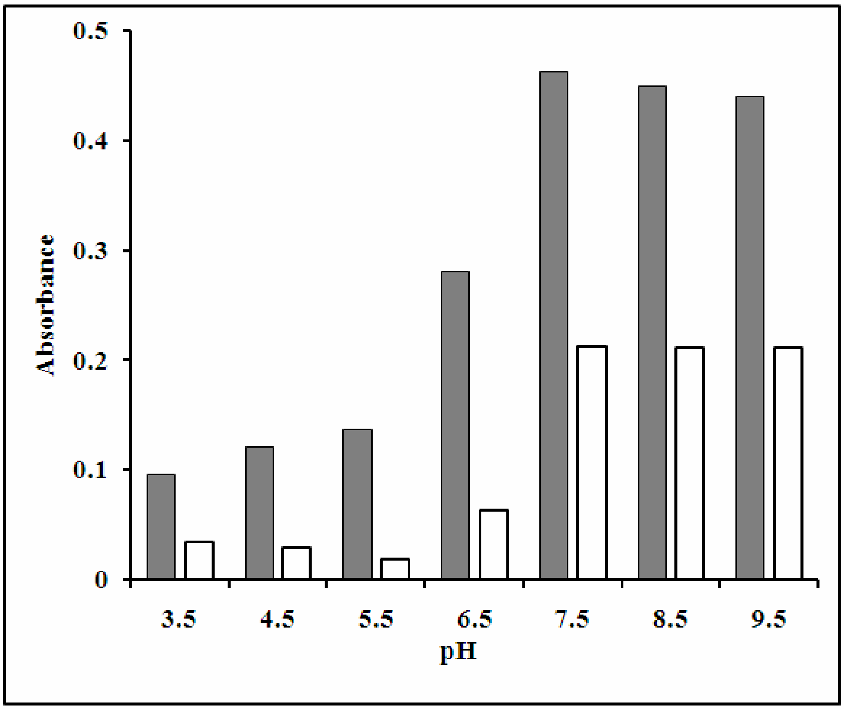
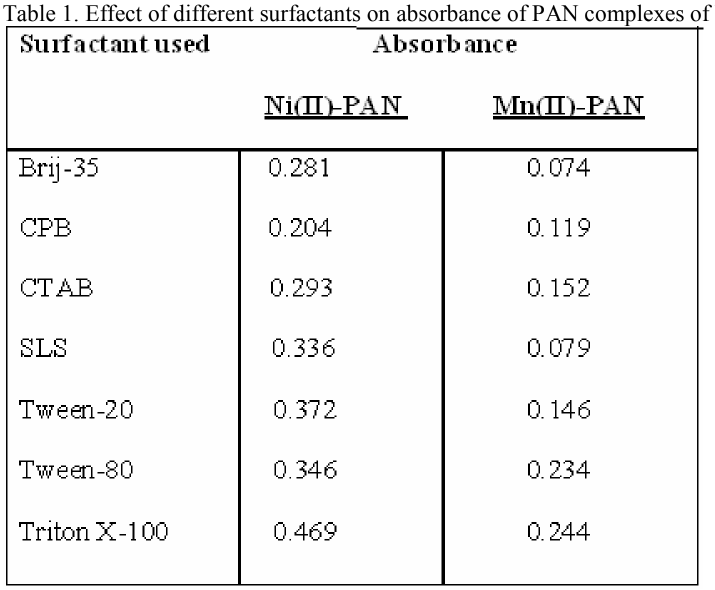


Figure 3. Effect of pH on the absorbance of (■) Ni(II)-PAN and (□) Mn(II)-PAN complex.

PAN complexes of Ni(II) and Mn(II) are insoluble in water, so various surfactants such as Tween-20, TritonX-100, cetylpyridinium bromide (CPB), cetyltrimethylammonium bromide (CTAB), and sodium dodecylsulfate (SDS) were tried as solublizing agents. Both for Ni(II)-PAN and Mn(II)-PAN complexes absorbance were maximum with Triton X-100 as given in Table 1. So, for simultaneous determination of Ni(II) and Mn(II) 2.5 mL of 1.0 % Triton X-100 was selected as the working micellizing agent for further studies.

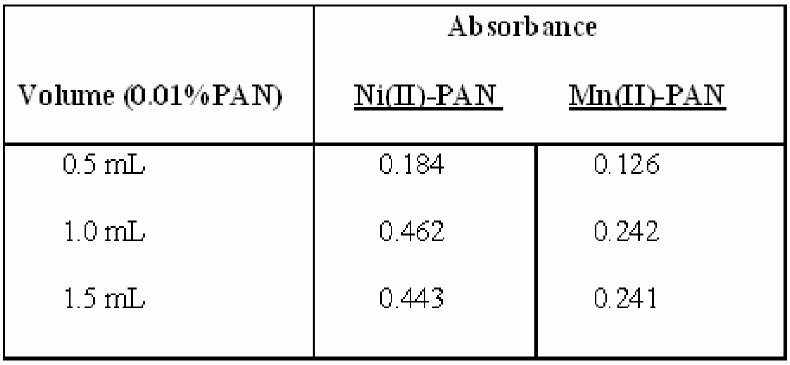
Table 1. Effect of different surfactants on absorbance of PAN complexes of Ni(II) and Mn(II).



Surfactant used	Absorbance	
	Ni(II)-PAN	Mn(II)-PAN
Brij-35	0.281	0.074
CPB	0.204	0.119
CTAB	0.293	0.152
SLS	0.336	0.079
Tween-20	0.372	0.146
Tween-80	0.346	0.234
Triton X-100	0.469	0.244

Effect of various amounts of reagent on the absorbance of Ni(II)-PAN and Mn(II)-PAN complexes was studied. As given in Table 2 the maximum absorbance in both the cases was observed when 1.0 mL of 0.01 % PAN was used for individual calibration. To ensure the complete complexation for simultaneous determination of Ni(II) and Mn(II), 2.0 mL of 0.01 % PAN was used.

Table 2. Effect of different volumes of 0.01 % PAN on absorbance of PAN complexes of Ni(II) and Mn(II).



Volume (0.01%PAN)	Absorbance	
	Ni(II)-PAN	Mn(II)-PAN
0.5 mL	0.184	0.126
1.0 mL	0.462	0.242
1.5 mL	0.443	0.241

3.2. StoichiomeTry of the Complexes

The composition of the complexes as established by Job's method of continuous variation and mole ratio method is found to be 1:2 (metal : ligand) both for Ni(II)-PAN and Mn(II)-PAN complexes.

3.3. Applying Kinetic-HPSAM

In this system, Ni(II) and Mn (II) are the analyte and interferent respectively. Difference in the rate of complex formation of Ni(II) and Mn(II) with PAN at pH 7.5 is the main reason for applying kinetic-HPSAM. The best pair of time (t_1 and t_2) selected is the one which gives greatest slope increment for Ni(II) and the change in absorbance (ΔA) for Mn(II) is negligible. For this reason the time pair 20 and 70 s was employed for obtaining the highest accuracy. H-point standard addition calibration curves are constructed at these two selected times (20 and 70 s) at a wavelength of 565 nm giving two straight lines that intersect at a common H-point with coordinates $-C_H$ and A_H, where $-C_H$ is the unknown Ni(II) concentration and A_H the analytical signal due to Mn(II). The concentration of Mn(II) was calculated from the analytical signal (A_H).

3.4. Reproducibility of the Method

Under optimum conditions simultaneous determination of Ni(II) and Mn(II) were made by using kinetic-HPSAM. To check the reproducibility of the method five replicate experiments were performed and the results are given in Table 3.

Table 3. Results of five replicate experiments for the analysis of Ni(II) and Mn(II) mixtures.

A-C Equation	r^2	Present (μg mL^{-1})		Found (μg mL^{-1})	
		Ni(II)	Mn(II)	Ni(II)	Mn(II)
$A_{20}=0.6419C_i+0.5856$	0.9977	0.620	0.280	0.625	0.278
$A_{70}=0.8451C_i+0.7125$	0.9953				
$A_{20}=0.6422C_i+0.5850$	0.9916	0.620	0.280	0.626	0.276
$A_{70}=0.8452C_i+0.7120$	0.9989				
$A_{20}=0.6105C_i+0.5692$	0.9952	0.620	0.280	0.609	0.275
$A_{70}=0.8445C_i+0.7119$	0.9950				
$A_{20}=0.6209C_i+0.5737$	0.9976	0.620	0.280	0.622	0.283
$A_{70}=0.8379C_i+0.7086$	0.9987				
$A_{20}=0.6411C_i+0.5554$	0.9934	0.620	0.280	0.621	0.281
$A_{70}=0.8503C_i+0.6853$	0.9964				
Mean				0.621	0.278
Standard deviation				0.006	0.003
R.S.D (%)				0.966	1.079
LOD				0.018	0.009
LOQ				0.06	0.03

3.5. Accuracy and Precision

Several synthetic samples with different concentration ratios of Ni(II) and Mn(II) were analyzed using kinetic-HPSAM. The results are given in Table 4. H-point standard addition plots for several synthetic samples are shown in Figures 4 and 5. From these graphs, concentration of Ni(II) is found to be independent of the concentration of Mn(II) and analytical signal of Mn(II) was found to be independent of Ni(II) concentration.

Table 4. Results of several experiments for the analysis of Ni(II) and Mn(II) in synthetic samples by Kinetic-HPSAM.

A-C Equation	r^2	Present (μg mL^{-1})		Found (μg mL^{-1})		% recovery	
		Ni(II)	Mn(II)	Ni(II)	Mn(II)	Ni(II)	Mn(II)
A_{20}=0.4107C_i+0.2128	0.9974	0.176	0.219	0.174	0.213	98.86	97.26
A_{70}=0.6742C_i+0.2586	0.9935						
A_{20}=0.5254C_i+0.3548	0.9952	0.411	0.219	0.404	0.214	98.29	97.72
A_{70}=0.7966C_i+0.4644	0.9884						
A_{20}=0.3284C_i+0.1977	0.9959	0.088	0.256	0.087	0.255	98.86	99.61
A_{70}=0.5106C_i+0.2136	0.9884						
A_{20}=0.5932C_i+0.4385	0.9891	0.469	0.256	0.461	0.248	98.29	96.87
A_{70}=0.8136C_i+0.5401	0.9973						
A_{20}=0.4068C_i+0.2122	0.9947	0.323	0.128	0.317	0.125	98.14	97.65
A_{70}=0.6525C_i+0.2902	0.9963						
A_{20}=0.7288C_i+0.4279	0.9899	0.323	0.293	0.322	0.291	99.69	99.32
A_{70}=0.9492C_i+0.4989	0.9861						
A_{20}=0.5508C_i+0.1387	0.9903	0.146	0.092	0.142	0.091	97.26	98.91
A_{70}=0.6913C_i+0.1586	0.9968						
A_{20}=0.6216C_i+0.2680	0.9981	0.146	0.275	0.144	0.269	98.63	97.82
A_{70}=0.7203C_i+0.2822	0.9817						

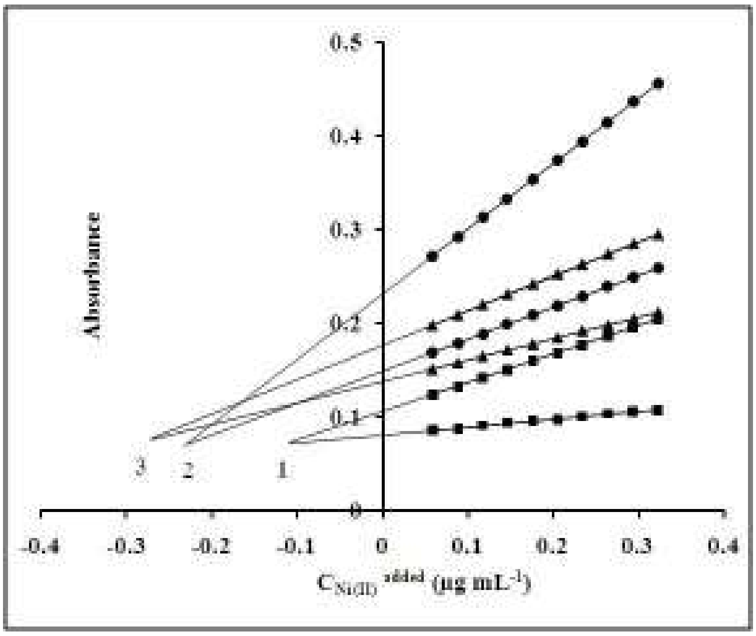


Figure 4. H-point standard addition plot for fixed Mn(II) concentration (0.109 µg mL^{-1}) and different Ni(II) concentrations of: (1) 0.114, (2) 0.233 and (3) 0.283 µg mL^{-1} under optimized conditions.

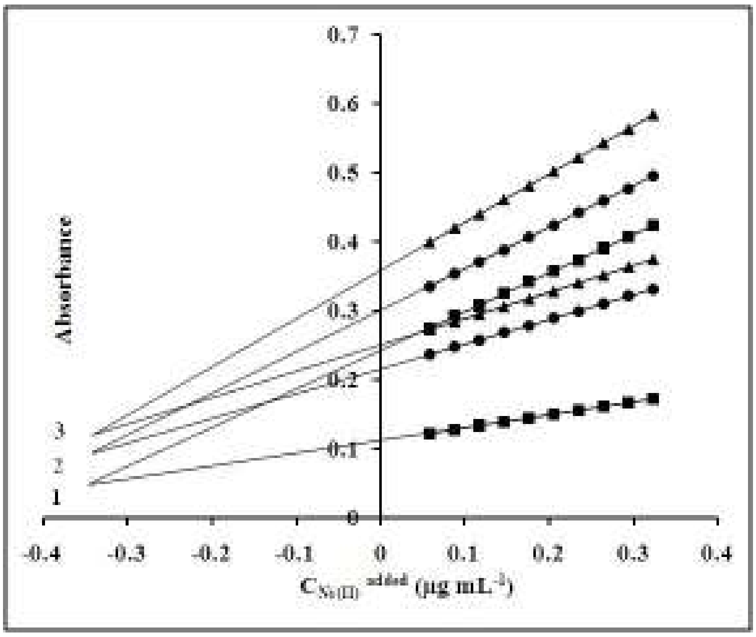
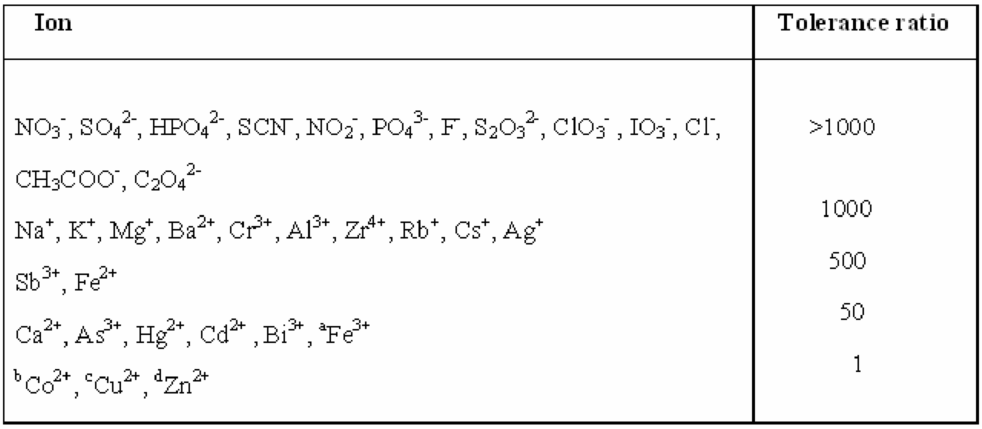


Figure 5. H-point standard addition plot for fixed Ni(II) concentration (0.352 µg mL^{-1}) and different Mn(II) concentrations of: (1) 0.070, (2) 0.136 and (3) 0.182 µg mL^{-1} under optimized conditions.

3.6. Effect of Diverse Ions

The effect of different ions on the simultaneous determination of 0.294 µg mL^{-1} each of Ni(II) and Mn(II) was studied by the developed method. The results are given in Table 5. Most of the ions did not interfere. Only Co(II), Cu(II) and Zn(II) interfered strongly. Co(II) could be masked by addition of potassium cyanide and oxidizing with hydrogen peroxide. Cu(II) can be masked with sodium thiosulfate, Fe(III) interference can be eliminated by the addition of ammonium oxalate and that of Zn(II) with sodium cyanide. The greatest interference is caused by the presence of Zn(II) in the sample solution.

Table 5. Tolerance ratio of foreign ions in the determination of Ni(II) and Mn(II).



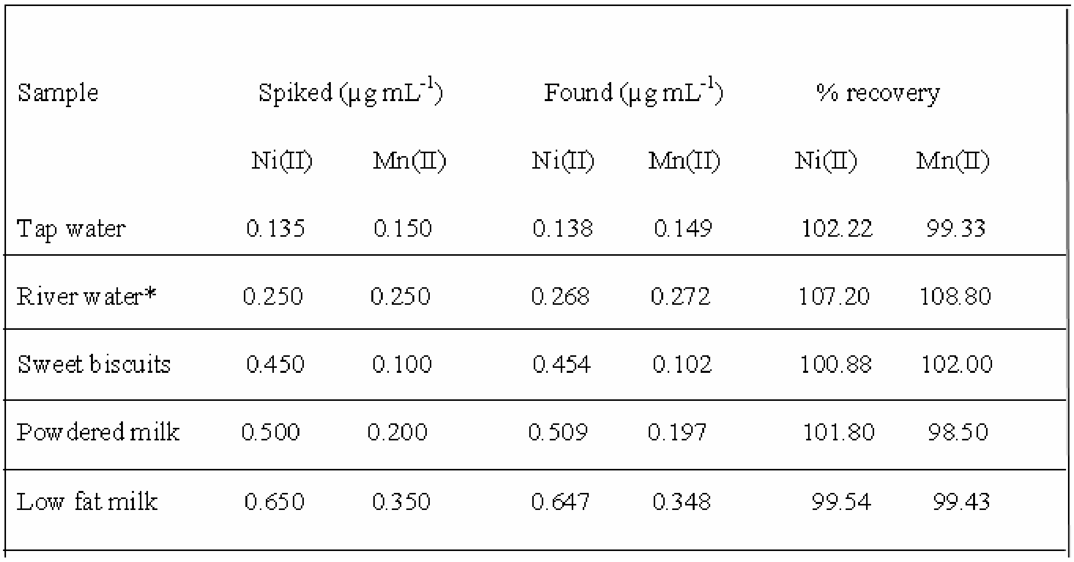
Ion	Tolerance ratio
NO_3^-, SO_4^{2-}, HPO_4^{2-}, SCN^-, NO_2^-, PO_4^{3-}, F^-, $S_2O_3^{2-}$, ClO_3^-, IO_3^-, Cl^-, CH_3COO^-, $C_2O_4^{2-}$	>1000
Na^+, K^+, Mg^+, Ba^{2+}, Cr^{3+}, Al^{3+}, Zr^{4+}, Rb^+, Cs^+, Ag^+	1000
Sb^{3+}, Fe^{2+}	500
Ca^{2+}, As^{3+}, Hg^{2+}, Cd^{2+}, Bi^{3+}, ${}^aFe^{3+}$	50
${}^bCo^{2+}$, ${}^cCu^{2+}$, ${}^dZn^{2+}$	1

a- Masked with ammonium oxalate; b- masking with potassium cyanide and then oxidized with hydrogen peroxide; c- masked with sodium thiosulfate; d- masked with sodium cyanide.

3.7. Application

The proposed method has successfully been applied for simultaneous determination of Ni(II) and Mn(II) in spiked tap water, river water (Sutlej) and synthetic samples that had compositions prepared according to some alloys. Ni(II) and Mn(II) determination by the proposed method was also done in sweet biscuits, powdered milk and low fat milk available locally. For this 1.0 g sample (biscuits, powdered or low fat milk) was spiked with known amounts of Ni(II) and Mn(II), digested with 12 mL mixture of $HNO_3 : H_2SO_4$ taken in 8:4 volume. The mixture was heated up to 130 °C for 1 h after cooling 5 mL of distilled water was added to the sample and mixed. The residue was filtered and diluted with distilled water. The spiked sample solution was then analyzed by the developed method. The results are given in Table 6 and 7. The good agreement between the obtained results and the known amounts present in the sample indicate the successful applicability of the method.

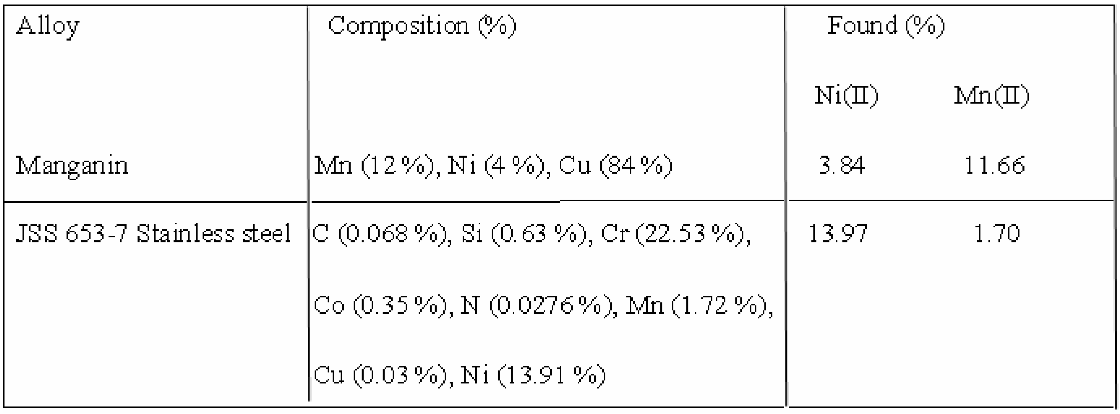
Table 6. Determination of Ni(II) and Mn(II) in different spiked samples by Kinetic-HPSAM.



Sample	Spiked (μg mL^{-1})		Found (μg mL^{-1})		% recovery	
	Ni(II)	Mn(II)	Ni(II)	Mn(II)	Ni(II)	Mn(II)
Tap water	0.135	0.150	0.138	0.149	102.22	99.33
River water*	0.250	0.250	0.268	0.272	107.20	108.80
Sweet biscuits	0.450	0.100	0.454	0.102	100.88	102.00
Powdered milk	0.500	0.200	0.509	0.197	101.80	98.50
Low fat milk	0.650	0.350	0.647	0.348	99.54	99.43

River water* - Sutlej, Punjab

Table 7. Determination of Ni(II) and Mn(II) in synthetic alloy samples.



Alloy	Composition (%)	Found (%)	
		Ni(II)	Mn(II)
Manganin	Mn (12 %), Ni (4 %), Cu (84 %)	3.84	11.66
JSS 653-7 Stainless steel	C (0.068 %), Si (0.63 %), Cr (22.53 %), Co (0.35 %), N (0.0276 %), Mn (1.72 %), Cu (0.03 %), Ni (13.91 %)	13.97	1.70

4. CONCLUSION

Simultaneous determination of Ni(II) and Mn(II) without the use of any expensive instrument has been done. This reduces the cost of applied method. No extraction step is required as determination has been done in micellar media and hence the use of toxic and carcinogenic organic solvents is avoided. Micellar systems solublized the insoluble complex, and eliminated the need of non-aqueous extraction step in analysis. This reduces the toxicity of the applied method.

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