
Chapter – 8

SIMULTANEOUS DERIVATIVE SPECTROPHOTOMETRIC DETERMINATION OF SOME METAL IONS

INTRODUCTION

The direct spectrophotometric determination of metal ions in multicomponent systems is often complicated by interferences from the formulation matrix and spectral overlapping. Such interferences have been treated in many ways, such as solving two simultaneous equations¹ or using absorbance ratios at certain wavelengths.²⁻⁴ However, during the application of these methods¹⁻⁴, the presence of spectral interferences or spectral overlap would certainly lead to erroneous results⁵. Other approaches aimed at solving this problem have been employed; including pH induced differential spectrophotometric⁶, least squares⁷ and orthogonal function⁸ methods.

Derivative spectrophotometry is a useful means of resolving two overlapping spectra and eliminating matrix interferences in the assay of two-component mixtures using the zero-crossing technique⁹⁻¹¹ (Fig. 8.1).

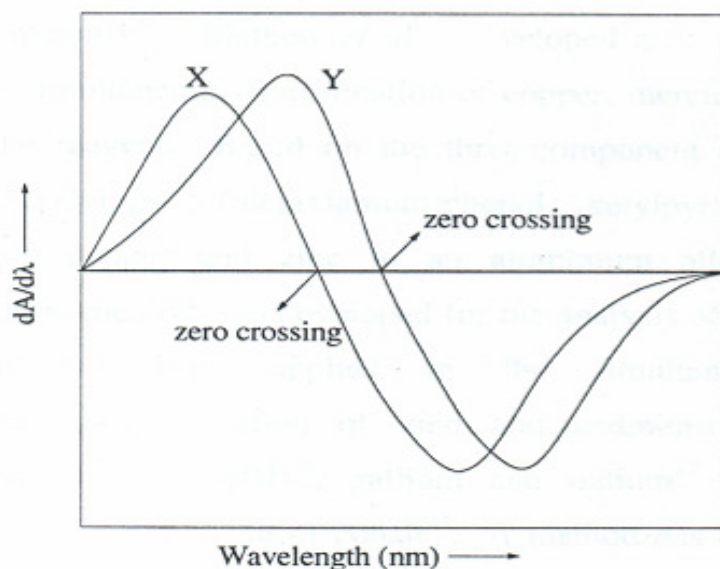


Fig.8.1: Use of zero-crossing technique to allow quantization of one chromophore (X) overlapped by the absorption band of another chromophore (Y)

In the absence of a zero-crossing point, two simultaneous equations can be solved to determine the components in such a mixture¹². The latter method is based on criteria for selecting the optimum working wavelengths². In addition, the component being determined should make a reasonable contribution to the total derivative reading of the mixture at the selected wavelength. Derivative spectrophotometric analysis of two-component mixtures is also carried out without the need to solve simultaneous equations. The compensation method¹³ is also used for the purpose. It is a non-mathematical method for the detection and elimination of unwanted absorption during photometric analysis. However, relatively few references are available in the literature on the determination of mixtures of metal ions by derivative spectrophotometry. Jiang, Chongqiu¹⁴ *et al.* established first derivative spectrophotometric method for the simultaneous determination of cobalt and iron. Murillo¹⁵ *et al.* reported a first derivative spectrophotometric method for the simultaneous determination of cobalt and nickel. A second derivative spectrophotometric method was proposed by Jimenez¹⁶ *et al.* for the simultaneous determination of cobalt and vanadium in alloy steels. Wang¹⁷ *et al.* reported a first derivative spectrophotometric method for the simultaneous determination of Fe (III) and Cu (II). A second derivative spectrophotometric method was developed for nickel and vanadium determination in petroleum and petroleum residues by Wang¹⁸ *et al.* The mixture of iron (II) and cobalt (II) was resolved by Salinas¹⁹ *et al.* using the second derivative spectrophotometry.

Bermejo-Barrera²⁰ *et al.* described the application of derivative spectrophotometry to the simultaneous determination of Cu (II) and Co (II) without solving the simultaneous equations. Zhuzi²¹ *et al.* determined chromium and manganese simultaneously by second derivative spectrophotometry. Cu (II) and Zn

(II) were determined continuously by Li, Huamin and Yan Junfeng²² using fourth derivative spectrophotometry. A first derivative spectrophotometric method was developed for the simultaneous determination of U (VI) and Th (IV) by Kuroda²³ *et al.* and Ramesh²⁴ *et al.*

A simultaneous first derivative spectrophotometric determination of Cu (II) and Co (II) was carried out by Vereda²⁵ *et al.* Pd (II) and Co (II) were determined simultaneously by derivative spectrophotometry by Perez²⁶ *et al.*

A simultaneous first derivative spectrophotometric determination of Co (II) and Fe (II) was carried out by Ritcher²⁷ *et al.*, and Toral²⁸ *et al.* Ozturk²⁹ *et al.* reported the simultaneous determination of Co (II) and Ni (II) by first derivative spectrophotometry. Ghasemi³⁰ *et al.* proposed first and second derivative spectrophotometric method for simultaneous determination of Co (II) and Ni (II). Kevser Sozgen³¹ *et al.* reported second derivative simultaneous spectrophotometric determination of Co (II), Ni (II) and Fe (II). Kolomiets³² *et al.* developed first and second derivative simultaneous spectrophotometric methods for the determination of Ni (II), Co (II) Cu (II) and Fe (II). A simultaneous first derivative spectrophotometric determination of Fe (II) and Ni (II) was carried out by Hashem³³ *et al.*

Toral³⁴ *et al.* reported a second derivative spectrophotometric determination of Ru and Fe. A simultaneous third derivative spectrophotometric determination of Ru and Os was carried out by Balcerzak³⁵ *et al.* A simultaneous first and second derivative spectrophotometric determination of Pt and Ru was carried out by Balcerzak³⁶ *et al.* V.K.Reddy³⁷ *et al.* developed a first derivative simultaneous spectrophotometric determination of Ni (II) and Fe (II). Grabaric³⁸ *et al.* proposed a first derivative simultaneous spectrophotometric determination of Ni (II) and Zn (II). Eskandari³⁹ *et al.* reported first and second derivative simultaneous

spectrophotometric determination of Co (II) and Pd (II). Bhalotra⁴⁰ et al. developed a first; derivative simultaneous spectrophotometric determination of Ni (II) and Pd (II). A simultaneous first derivative spectrophotometric determination of V and U was reported by Abbsa⁴¹ et al., Hussain Reddy⁴² et al developed a first derivative simultaneous spectrophotometric determination of Ni (II) and Cu (II). A first derivative simultaneous spectrophotometric determination of V (V) and Cu (II) was developed by Krishna Reddy⁴³ *et al.* A first order derivative spectrophotometry for simultaneous determination of Mo (VI) and Ti (IV) was reported by Babaiah⁴⁴ *et al.* A simple simultaneous fourth derivative spectrophotometric method was reported for the analysis of cobalt (II) and nickel (II) by Praveen Kumar⁴⁵ *et al.*, Lakshmi narayana⁴⁶ *et al* developed direct simultaneous spectrophotometric method is proposed for the analysis of chromium (VI) and vanadium (V).

A simultaneous second order derivative spectrophotometric method was proposed for the analysis of two-component system containing Indium (III) and Vanadium (IV) by I. Sreevani⁴⁷ *et al.*, a simultaneous third order derivative spectrophotometric method of determination of iron (II) and uranium (VI) was reported by V.S Anusuya Devi⁴⁸ *et al.*, Mallikarjuna⁴⁹ *et al* reported the simultaneous second order derivative spectrophotometric determination of gallium (III) and aluminium (III). Sumathi⁵⁰ *et al* reported simultaneous determination of zirconium (IV) and titanium (IV). Prem Kumar^{51,52} *et al.* developed simultaneous second order derivative methods for determination of Au (III), Co (II) and iron (III), nickel (II).

The author has employed 2-AAINH to develop derivative spectrophotometric methods for the simultaneous determination of mixtures of metal ions. The results of the present investigations are reported in this chapter.

Section i : Simultaneous first order derivative spectrophotometric determination of Manganese (II) and Nickel (II)

An attempt has been made in the present thesis to develop a simple and selective first order derivative spectrophotometric method for the simultaneous determination of Mn (II) and Ni (II) in a mixture. The derivative spectrum of Mn (II) complex with 2-AAINH shows zero amplitude at 437 nm and considerably large amplitude at 447 nm. On the other hand Ni (II) complex with 2-AAINH shows sufficient amplitude at 485 nm with zero amplitude at 447 nm. Further, the derivative amplitudes obey Beer's law at 447 nm and 485 nm for Mn (II) and Ni (II) respectively. Hence, Mn (II) and Ni (II) can be determined simultaneously in a mixture without separation by measuring the first order derivative amplitudes at 447 nm and 485 nm respectively.

Simultaneous determination of Mn (II) and Ni (II)

Different aliquots of solutions containing 0.2746-2.5 $\mu\text{g mL}^{-1}$ of Mn (II) and 0.2342 to 2.0 $\mu\text{g mL}^{-1}$ of Ni (II) were transferred in to a series of 10 ml standard flasks. 4 ml of buffer solution (pH-9.0) and 1.0 ml of 2-AAINH ($1 \times 10^{-2}\text{M}$) were added to each of these flasks and diluted up to the mark with distilled water and the first derivative spectra were recorded in the range 350 - 600 nm (Fig. 8.i.1).

Verification of Beer's law validity

Individual calibration plots were constructed by plotting the first derivative amplitudes measured at 447 nm against the amount of Mn (II) and those measured at 485 nm against the amount of Ni (II) and shown in Figs. 8.i.2 and 8.i.3 respectively. The plots indicate that Beer's law is obeyed in the range 0.056–8.65 $\mu\text{g mL}^{-1}$ of Mn(II) and 0.045 -3.25 $\mu\text{g mL}^{-1}$ of Ni (II).

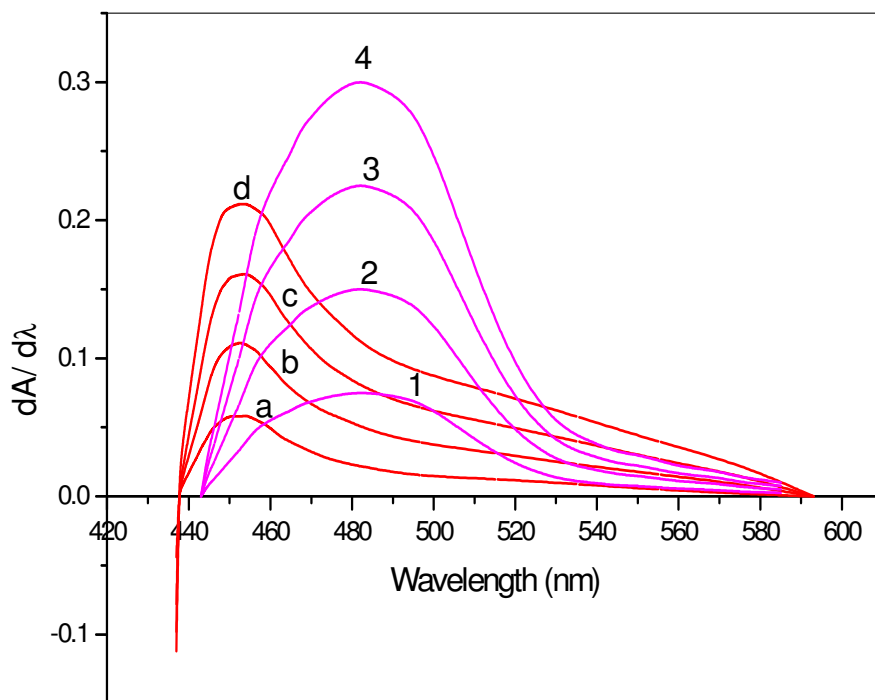


Fig. 8.i.1 : First derivative spectra of [Mn(II)-2-AAINH], [Ni(II)-2-AAINH] at different concentrations
 Mn(II) ($\mu\text{g mL}^{-1}$) = (a) 0.2746; (b) 0.5492; (c) 0.8238; (d) 1.0984
 Ni(II) ($\mu\text{g mL}^{-1}$) = (1) 0.2342; (2) 0.4694; (3) 0.7041; (4) 0.9888

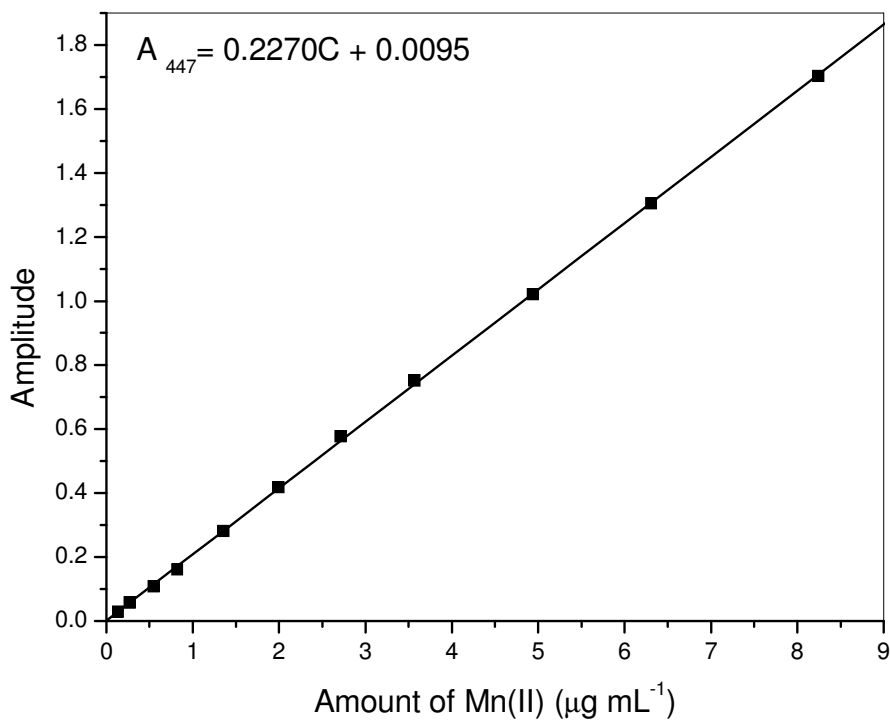


Fig. 8.i.2 : First derivative amplitude Vs amount of Mn(II)
 $\lambda = 447\text{nm}$; $\text{pH} = 9.0$

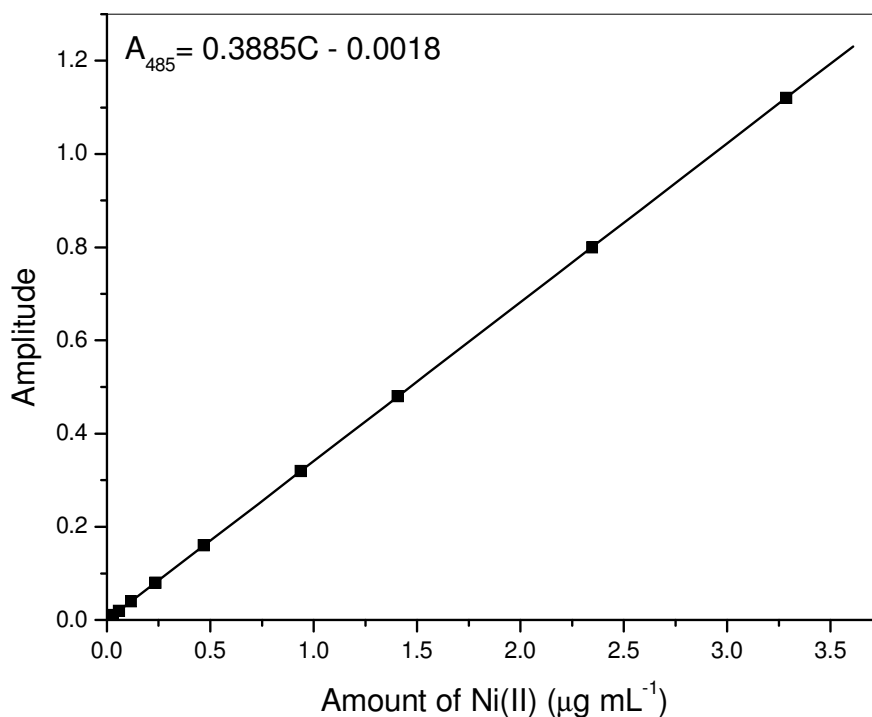


Fig. 8.i.3. : First derivative amplitude Vs amount of Ni(II)
 [2-AAINH] = 8×10^{-4} M
 $\lambda = 485\text{nm}$; pH = 9.0

The validity of the proposed simultaneous method was tested by determining Manganese and Nickel in various binary mixtures containing different known amounts of manganese and nickel. The results obtained are shown in Table.8.i.1. The results in table indicate quantitative recovery of both metal ions.

Table 8.i.1

Simultaneous first order derivative determination of Mn (II) and Ni (II)

Amount taken ($\mu\text{g mL}^{-1}$)		Amount found* ($\mu\text{g mL}^{-1}$)		Recovery (%)	
Mn (II)	Ni (II)	Mn (II)	Ni (II)	Mn (II)	Ni (II)
0.2746	0.2342	0.2736	0.2336	99.63	99.74
0.2746	0.2342	0.2699	0.238	98.28	101.62
0.2746	0.2342	0.2785	0.2365	101.42	100.98
0.5492	0.4694	0.5485	0.4705	99.87	100.23
0.5492	0.4694	0.5520	0.4685	100.5	99.80
0.8238	0.7041	0.8315	0.7105	100.93	100.90
1.0984	0.9888	1.091	0.9800	99.32	99.11

* Average of five determinations

Application

The present simultaneous method was employed for the determination of amounts of manganese and nickel in some aluminium based samples. The sample solutions were prepared by dissolving an appropriate amount of the sample as described in chapter 3s.

A known aliquot of the aluminum based sample was treated with 5 ml of buffer solution (pH 9.0), 1.0 ml of 2-AAINH (1×10^{-2} M) and made up to the mark in a 10 ml volumetric flask with distilled water. The first derivative curve was recorded and the derivative amplitudes were measured at 447 nm and 485 nm. The amounts of manganese and nickel were computed from the measured amplitudes with the help of predetermined calibration plots. The results obtained are given in Table 8.i.2

Table 8.i.2
Simultaneous determination of Mn (II) and Ni (II) in aluminum based alloys

Sample	Certified Value (%)		Amount found by Present method* (%)		Recovery (%)		Relative error (%)	
	Mn (II)	Ni (II)	Mn (II)	Ni (II)	Mn (II)	Ni (II)	Mn (II)	Ni (II)
BAS-20 ^a	0.19	1.93	0.188	1.928	98.94	99.89	- 1.05	-0.10
BAS-85 ^b	0.02	0.91	0.0202	0.912	101.0	100.21	+1.0	+0.21

* Average of five determinations

Compositions (%)

a. Cu 4.10%; Ni 1.93%; Fe 0.43%; Mn 0.19%; Si 0.29%; Mg 1.61%; Rest

b. Cu 0.90%; Ni 0.91%; Fe 1.15%; Mn 0.02%; Si 2.04%; Mg 0.18%; Zn 0.01%; Rest Al

Section ii : Simultaneous first order derivative spectrophotometric determination of Nickel (II) and Cobalt (II)

The first order derivative spectra of Nickel (II) complex with 2-AAINH shows maximum amplitude at 480 nm, while Co (II) complex with 2-AAINH shows zero amplitude. On the other hand [Co(II)-2-AAINH] complex shows maximum absorbance at 530nm, while [Ni(II)-2-AAINH] complex shows low amplitude. Further, the derivative amplitudes obey Beer's law at 480 nm and 530 nm for Ni (II) and Co (II) respectively. Hence Ni (II) and Co (II) can be determined simultaneously in a mixture without separation by measuring the first order derivative amplitudes at 480 nm and 530 nm respectively.

Simultaneous determination of Ni (II) and Co (II)

To different aliquots containing Ni (II) and Co (II) in variable proportions were transferred in to a series of 10 ml standard flasks. 4 ml of buffer solution (pH-9.0) and 1.0 ml of 2-AAINH (1×10^{-2} M) were added and made up to the mark with distilled water. The first derivative spectra were recorded for these solutions in the range 350 nm – 600 nm and presented in Fig. 8.ii.1. The derivative amplitudes at 480 nm and 530 nm were measured and the amounts of Ni (II) and Co (II) present in the mixture were determined from predetermined calibration graph. The results obtained are shown in Table 8.ii.1. The results in table indicate quantitative recovery of both metal ions.

Individual plots were constructed by plotting the first derivative amplitudes measured at 480 nm against the amount of Ni (II) and those measured at 530 nm against the amount of Co (II) and shown in Figs. 8.ii.2 and 8.ii.3 respectively. The plots shows Beer's law is obeyed in the range $0.05\text{--}3.15 \mu\text{g mL}^{-1}$ of Ni (II) and $0.04\text{--}7.2 \mu\text{g mL}^{-1}$ of Co (II).

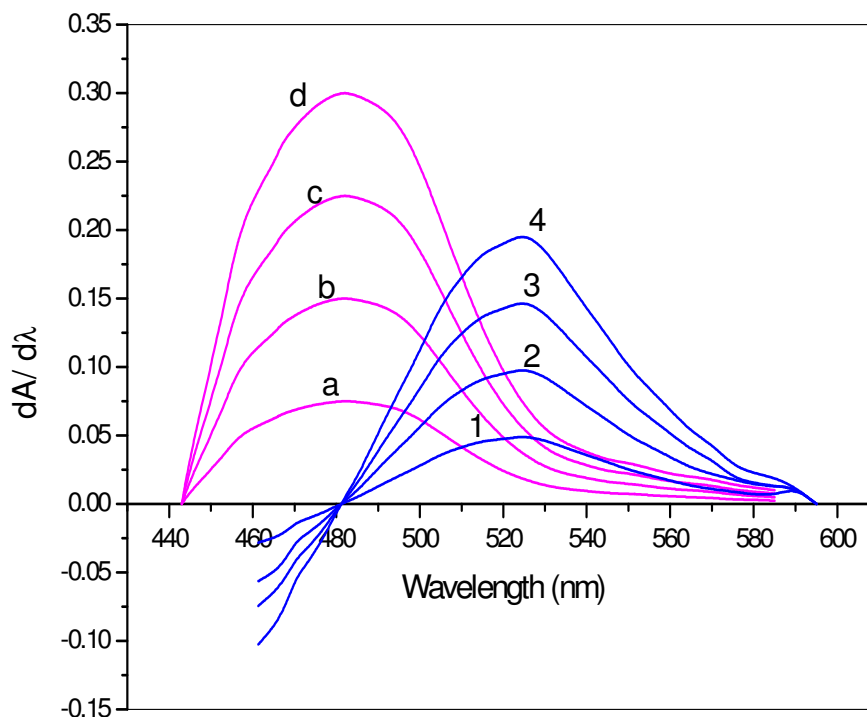


Fig. 8.ii.1 : First derivative spectra of [Ni(II)-2-AAINH], [Co(II)-2-AAINH] at different concentrations
 Ni(II) ($\mu\text{g mL}^{-1}$) = (a) 0.2342; (b) 0.4694; (c) 0.7041; (d) 0.9888
 Co(II) ($\mu\text{g mL}^{-1}$) = (1) 1.176; (2) 2.356; (3) 3.530; (4) 4.712

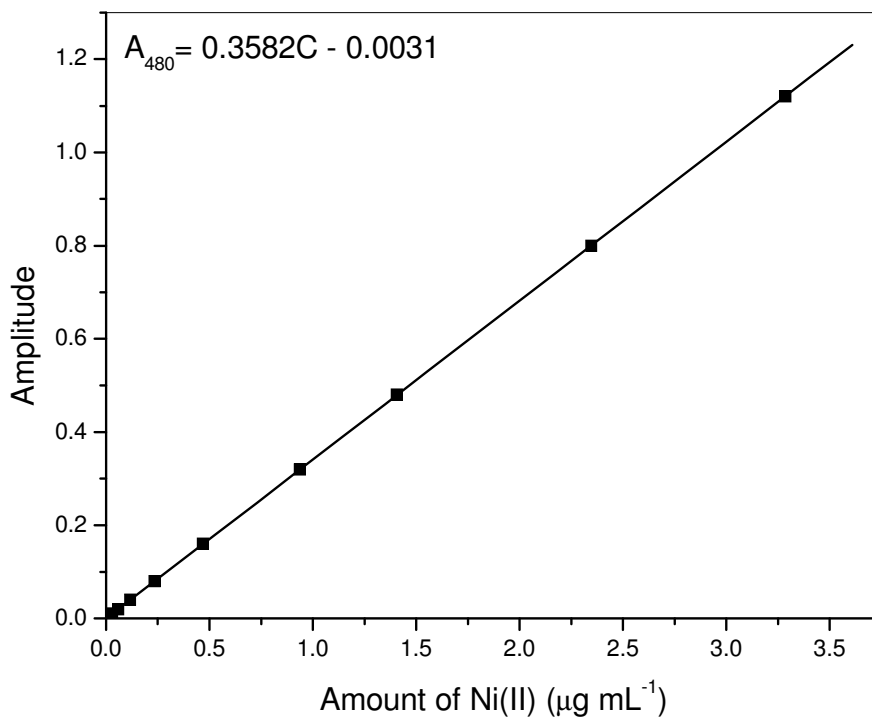


Fig. 8.ii.2 : First derivative amplitude Vs amount of Ni(II)
 [2-AAINH] = 8×10^{-4} M
 $\lambda = 480\text{nm}$; pH = 9.0

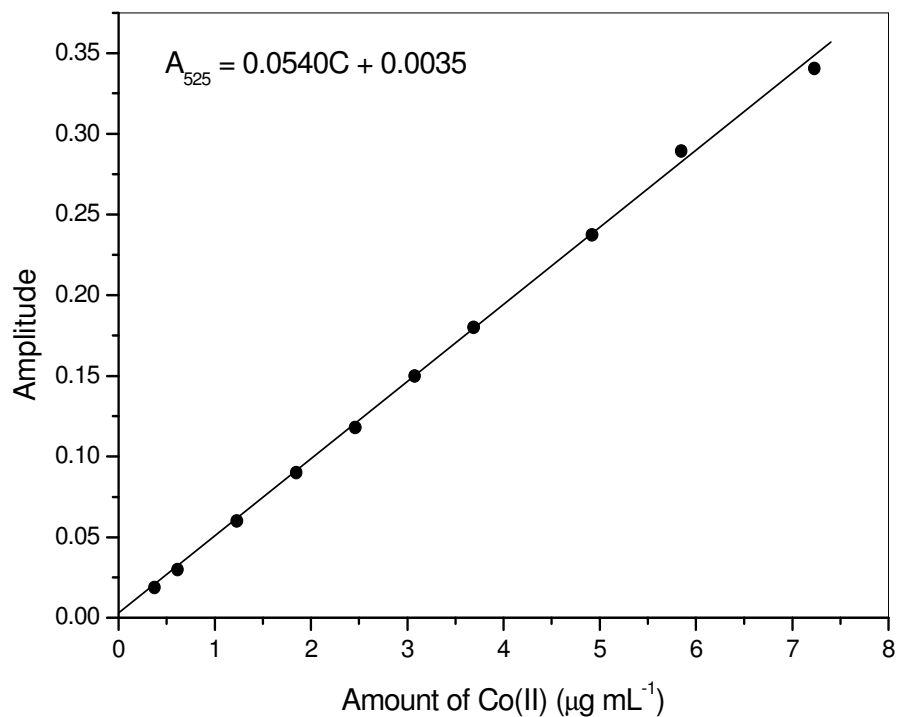


Fig. 8.ii.3 : First derivative amplitude Vs amount of Co(II)
 [2-AAINH] = 8×10^{-4} M
 $\lambda = 530$ nm ; pH = 9.0

Table 8.ii.1

Simultaneous first order derivative determination of Ni (II) and Co (II)

Amount taken ($\mu\text{g mL}^{-1}$)		Amount found* ($\mu\text{g mL}^{-1}$)		Recovery (%)	
Ni (II)	Co (II)	Ni (II)	Co (II)	Ni (II)	Co (II)
0.2342	1.176	0.2344	1.179	100.08	100.25
0.2342	1.176	0.2349	1.175	100.29	99.91
0.2342	1.176	0.2340	1.168	99.91	99.31
0.4694	2.356	0.4699	2.346	100.1	99.57
0.7041	2.356	0.7036	2.350	99.92	99.74
0.9888	4.712	0.9898	4.714	100.1	100.04

* Average of five determinations

Application

The present method was applied for the analysis of some alloy steel samples. The steel samples were brought into solution by employing the general procedure 31. The results obtained are presented in Table 8.ii.2.

Table 8.ii.2
Simultaneous determination of Ni (II) and Co (II) in alloy steel samples

Sample	Certified Value (%)		Amount found by Present method* (%)		Recovery (%)		Relative error (%)	
	Ni (II)	Co (II)	Ni (II)	Co (II)	Ni (II)	Co (II)	Ni (II)	Co (II)
Eligiloy M-17/2 ^a	15.00	40.00	14.95	40.10	99.66	100.25	-0.33	+0.25
BCS 406/1 ^b	0.140	0.016	0.142	0.0158	102.85	98.75	+1.42	-1.25

* Average of five determinations

a = 20% Cr; 40% Co; 15% Ni; 0.15% C; 15% Fe; 2% Mn; 7% Mo; 0.05% Be.

b = 0.066% Mn; 1.06% Cr; 0.05% Mo; 0.14% Ni; 0.016% Co; 0.091% Cu; 0.19% V.

Section iii: Simultaneous first order derivative spectrophotometric determination of molybdenum (VI) and vanadium (V)

Molybdenum (VI) and Vanadium (V) react with 2-AAINH forming coloured complexes and both have maximum intensities at pH 3.0. It is noticed that at pH 3.0 the first derivative spectra of Mo (VI) and V (V) complexes show maximum amplitude at 422 and 465 nm respectively. Studies are therefore carried out for the simultaneous determination of Mo (VI) and V (V) by first derivative spectrophotometric by measuring the derivative amplitudes at 422 and 465 nm respectively.

Simultaneous determination of Mo (VI) and V (V)

In a series of 10 ml standard flasks, different aliquots of solutions containing 0.4797-2.4 $\mu\text{g mL}^{-1}$ of Mo(VI) and 1.018 to 3.0 $\mu\text{g mL}^{-1}$ of V(V), 4.0 ml of buffer solution (pH-3.0) and 1.0 ml of 2-AAINH ($1 \times 10^{-2}\text{M}$) were added and diluted up to the mark with distilled water. The first derivative spectra were recorded in the range 380 nm -500 nm and shown in Fig. 8.iii.1. The figure indicates that Molybdenum shows maximum amplitude at 422 nm with low amplitude at 465 nm, while on vanadium shows maximum at 465 nm with zero crossing at 435 nm.

Verification of Beer's law validity

To establish the linear relationship between the amplitude and concentration of Mo (VI) at 422 nm and V (V) at 465 nm, Calibration plots were constructed by plotting the first derivative amplitudes measured at 422 nm against the amount of Mo (VI) and those measured at 465 nm against the amount of V (V) and shown in Figs. 8.iii.2 and 8.iii.3 respectively. The plots indicate that Beer's law is obeyed in the range 0.15–7.45 $\mu\text{g mL}^{-1}$ of Mo (VI) and 0.25 -5.25 $\mu\text{g mL}^{-1}$ of V (V).

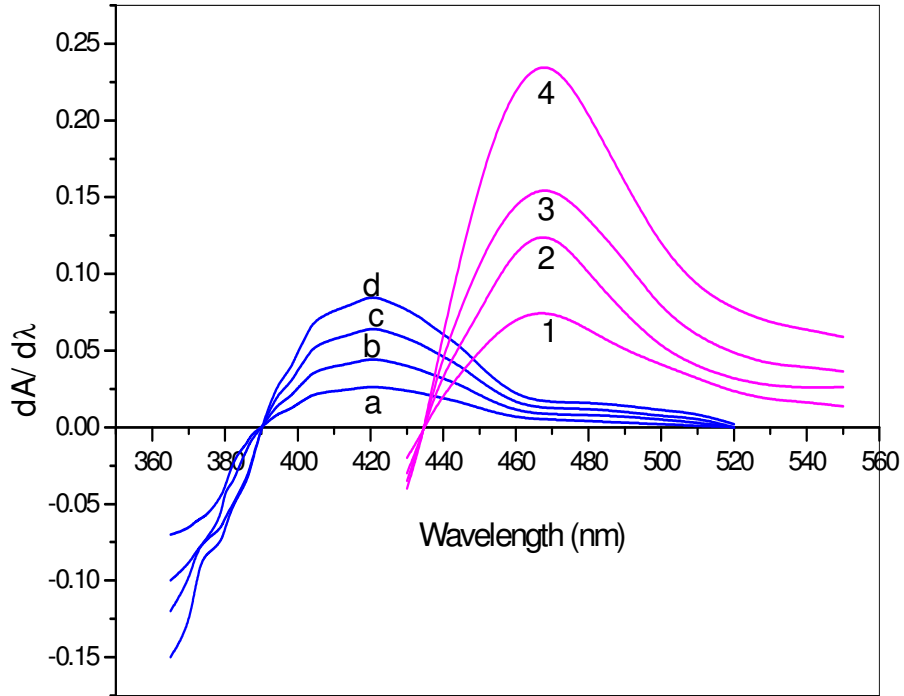


Fig. 8.iii.1 : First derivative spectra of [Mo(VI)-2-AAINH], [V(V)-2-AAINH] at different concentrations
 Mo(VI) ($\mu\text{g mL}^{-1}$) = (a) 0.4797; (b) 0.9594; (c) 1.4391; (d) 1.9188
 V(V) ($\mu\text{g mL}^{-1}$) = (1) 1.018; (2) 2.036; (3) 3.054; (4) 4.075

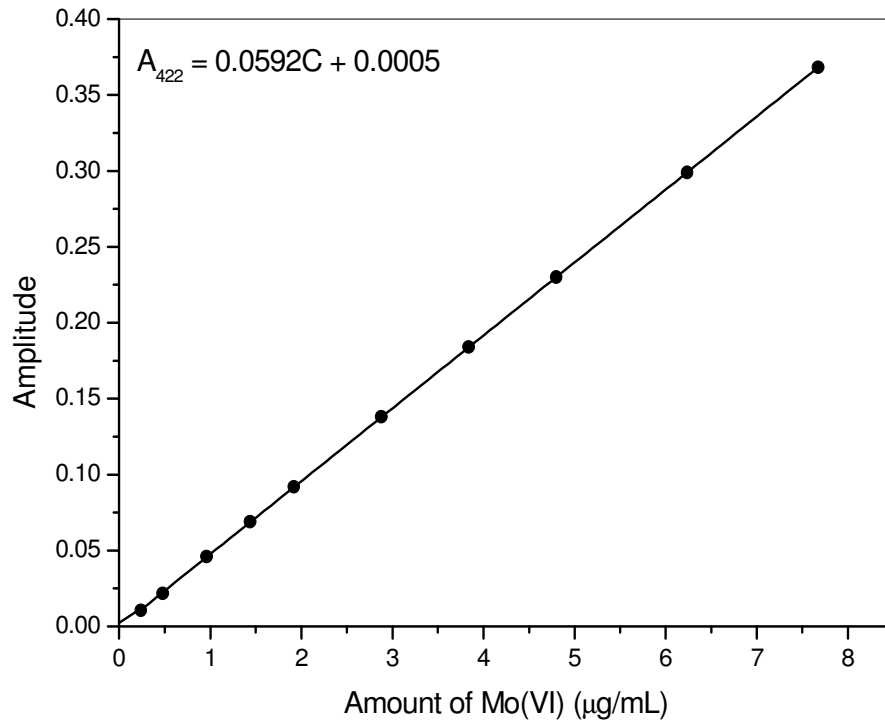


Fig. 8.iii.2 : First derivative amplitude Vs amount of Mo(VI)
 [2-AAINH] = 1×10^{-3} M
 $\lambda = 422$ nm ; pH = 3.0

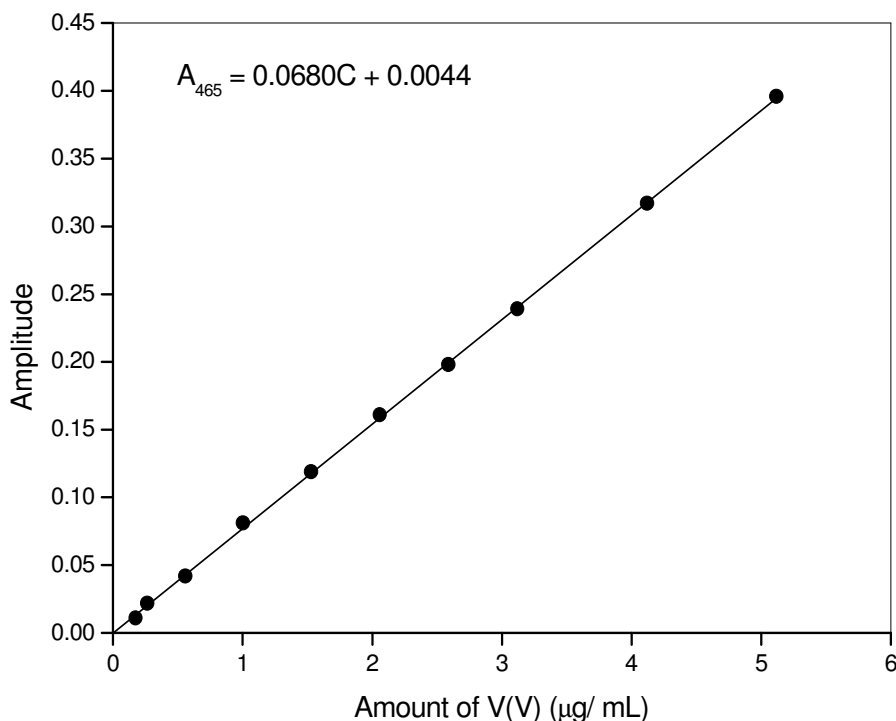


Fig. 8.iii.3 : First derivative amplitude Vs amount of V(V)
 [2-AAINH] = 1×10^{-3} M
 $\lambda = 465$ nm ; pH = 3.0

To investigate the validity and versatility of the proposed simultaneous method, a series of five test solutions containing different amounts of molybdenum and vanadium were prepared and analyzed by proposed derivative procedure. The results in Table.8.iii.1 indicate quantitative recovery of both metal ions.

Table 8.iii.1

Simultaneous first order derivative determination of Mo (VI) and V (V)

Amount taken ($\mu\text{g mL}^{-1}$)		Amount found * ($\mu\text{g mL}^{-1}$)		Recovery (%)	
Mo (VI)	V (V)	Mo (VI)	V (V)	Mo (VI)	V (V)
0.4795	1.015	0.4792	1.013	99.93	99.80
0.4795	1.015	0.4798	1.018	100.06	100.29
0.4795	1.015	0.4802	1.011	100.14	99.60
0.9594	1.527	0.9591	1.530	99.96	100.19
0.9594	1.527	0.9599	1.522	100.05	99.67
1.4391	2.036	1.4387	2.031	99.97	99.75
1.9188	2.545	1.9182	2.548	99.96	100.11

* Average of five determinations.

Applications

The present simultaneous method was employed for the determination of amounts of molybdenum and vanadium in some alloy steels. The steel samples were brought into solution by employing the general procedure 3I.

A known aliquot of the steel sample was treated with 4.0 ml of buffer solution (pH 3.0), 1.0 ml of 2-AAINH (1×10^{-2} M) and made up to the volume in a 10 ml volumetric flask with distilled water. The first derivative curve was recorded and the derivative amplitudes were measured at 422 nm and 465 nm. The amounts of Mo (VI) and V (V) were computed from the measured amplitudes with the help of pre-determined calibration plots. The results obtained are given in Table 8.iii.2.

Table 8.iii.2

Simultaneous determination of Mo (VI) and V (V) in alloy steel samples

Sample	Certified Value (%)		Amount found by Present method* (%)		Recovery (%)		Relative error (%)	
	Mo (VI)	V (V)	Mo (VI)	V (V)	Mo (VI)	V (V)	Mo (VI)	V (V)
BCS 406 ^a	1.030	0.02	1.027	0.0203	99.70	101.50	-0.29	+1.5
BCS 483 ^b	0.17	0.54	0.1708	0.537	100.47	99.44	+0.47	-0.55
NBS 362 ^c	0.068	0.04	0.0685	0.0398	100.73	99.50	+0.73	-0.50

* Average of five determinations.

a = Mn 0.53%; Ni 1.69%; Mo 1.03%; V 0.02%; Cr 2.12%; Cu 0.32%

b = W 10.8%; Cr 3.21%; V 0.54%; Mn 0.29%; Mo 0.17%; Co 1.94%; Rest Fe.

c = Mo 0.068%; C 0.16%; Mn 1.04%; Si 0.39%; V 0.04%; Ti 0.084%; W 0.20%; Sn 0.016%; Al 0.09%; Zr 0.19%; Sb 0.013%; Cu 0.5%; Cr 0.59%; Co 0.30%; As 0.09%.

Section iv: Simultaneous second order derivative spectrophotometric determination of manganese (II) and nickel (II)

The reagent, 2-AAINH reacts with manganese (II) forming greenish colored complex [Mn (II)- 2-AAINH] and with nickel (II) forming yellow-colored complex [Ni(II)- 2-AAINH] at pH 9.0. The second order derivative spectra of Manganese and nickel complexes at pH 9.0 were recorded in the wavelength region 400 – 600 nm and shown in Fig. 8.iv.1. From figure 8.iv.1, it was found that the second order derivative spectrum of Mn (II) complex shows zero amplitudes at 445 and 490 nm and considerably large amplitude at 462 nm. On the other hand, Ni (II) complex with 2-AAINH shows sufficient amplitude at 445 nm (valley), 482 nm (peak) and zero amplitude at 462 nm. The experimental results indicate the derivative amplitudes obey Beer's law at 462 and 445 nm or 482 nm for Mn (II) and Ni (II), respectively. Therefore, Mn (II) and Ni (II) can be determined simultaneously in a mixture without separation by measuring the second order derivative amplitudes at 462 nm and 445nm or 482 nm, respectively.

Verification of Beer's law validity

Beer's law plots were constructed for Mn (II) and Ni (II) complexes by measuring the second derivative amplitudes for variable amounts of Mn (II) at 462 nm and Ni (II) at 445 nm or 482 nm. The plots were shown in Figs. 8.iv.2 and 8.iv.3 for Mn (II) and Ni (II) respectively. The Beer's law was obeyed in the range 0.065 – 7.965 $\mu\text{g mL}^{-1}$ of Mn (II) and 0.07-3.5 $\mu\text{g mL}^{-1}$ of Ni (II).

Simultaneous determination of Mn (II) and Ni (II)

To different aliquots containing Mn (II) and Ni (II) in variable proportions in 10ml volumetric flasks, 4ml of buffer solution (pH 9.0), 1.0 ml of 2-AAINH (1×10^{-2} M) were added and made up to the mark with distilled water. The second derivative curves were recorded (Fig.8.iv.1) for these solutions.

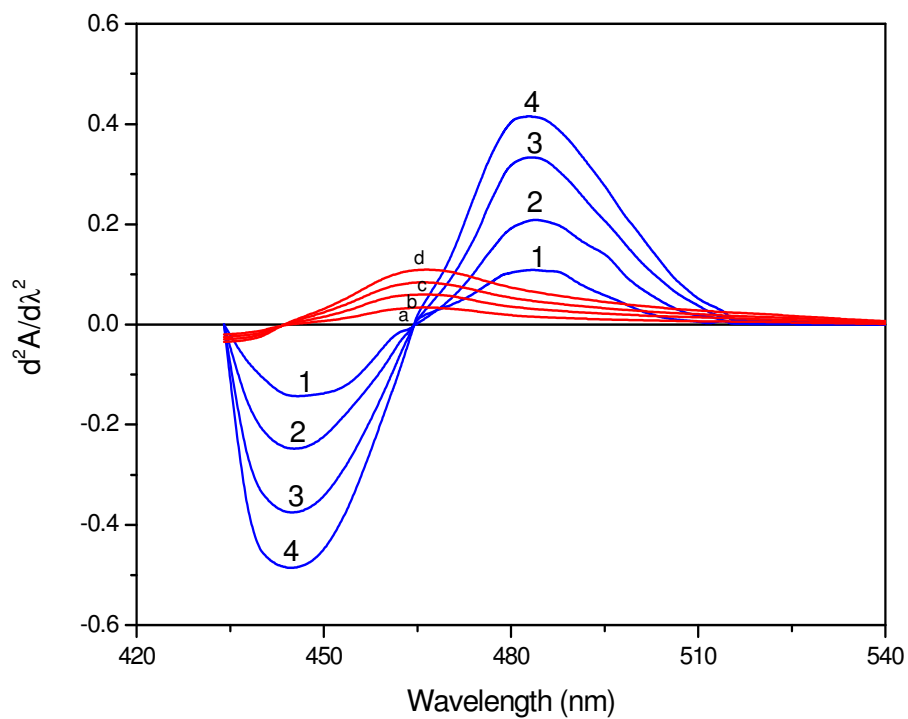


Fig. 8.iv.1 : Second derivative spectra of [Mn(II)-2-AAINH], [Ni(II)-2-AAINH] at different concentrations
Mn(II) ($\mu\text{g mL}^{-1}$) = (a) 0.2746; (b) 0.5492; (c) 0.8238; (d) 1.0984
Ni(II) ($\mu\text{g mL}^{-1}$) = (1) 0.2342; (2) 0.4694; (3) 0.7041; (4) 0.9888

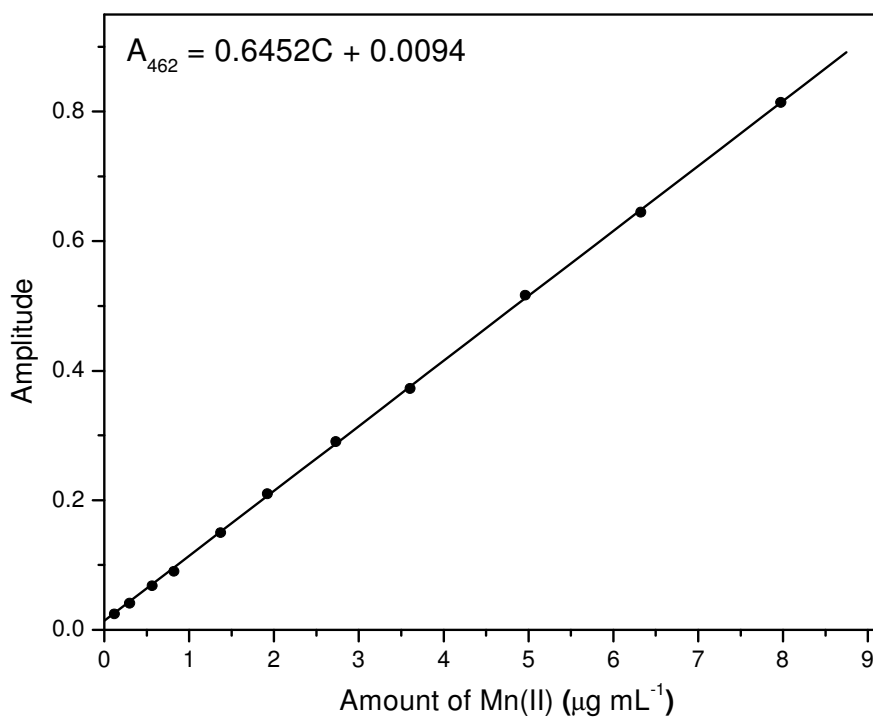


Fig. 8.iv.2 : Second derivative amplitude Vs amount of Mn(II)
[2-AAINH] = 1×10^{-3} M
 $\lambda = 462$ nm ; pH = 9.0

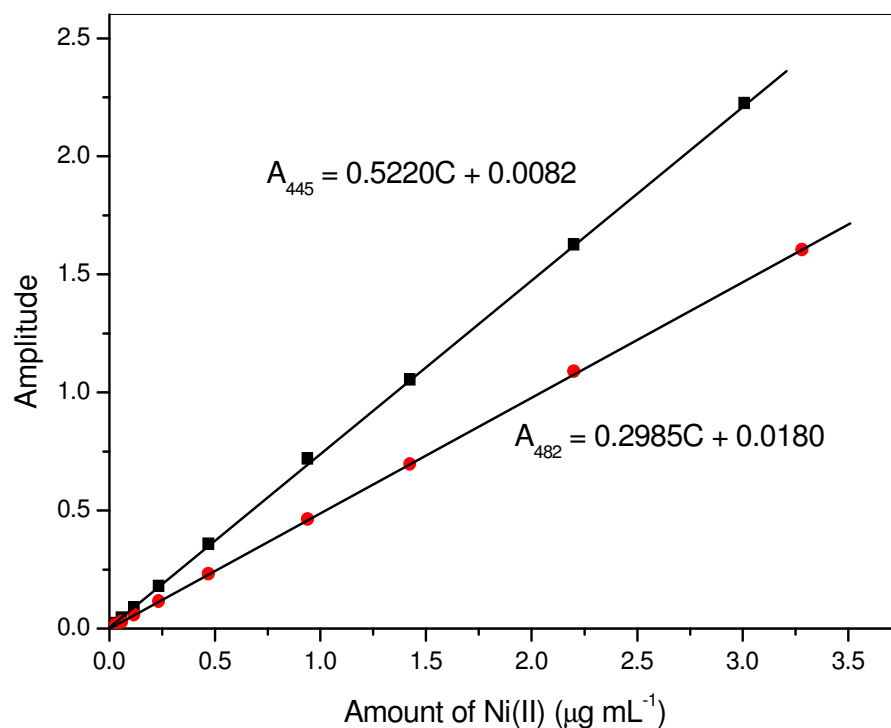


Fig. 8.iv.3 : Second derivative amplitude Vs amount of Ni(II)
 [2-AAINH] = 8×10^{-4} M
 $\lambda = 445 \text{ nm \& } 482 \text{ nm ; pH = 9.0}$

The derivative amplitudes at 462 nm and 445 nm or 482 nm were measured and the amounts of Mn (II) and Ni (II) present in the mixture were determined from predetermined calibration graphs. The results obtained are shown in Table 8.iv.1.

Table 8.iv.1

Simultaneous second order derivative determination of Mn (II) and Ni (II)

Amount taken (µg mL ⁻¹)		Amount found (µg mL ⁻¹)		Recovery (%)	
Mn (II)	Ni (II)	Mn (II)	Ni (II)	Mn (II)	Ni (II)
0.2746	0.2342	0.2743	0.2339	99.89	99.74
0.2746	0.2342	0.2750	0.2345	100.14	100.12
0.2746	0.2342	0.2748	0.2340	100.07	99.91
0.2746	0.2342	0.2747	0.2346	100.03	100.17
0.5492	0.4694	0.5494	0.4696	100.03	100.04
0.5492	0.4694	0.5489	0.4691	99.94	99.93
0.8238	0.7041	0.8235	0.7038	99.96	99.95
1.0984	0.9888	1.0987	0.9891	100.02	100.03

* Average of five determinations.

Application

The present simultaneous method was employed for the determination of amounts of manganese and nickel in some alloy steel and aluminium based alloy samples. The steel sample and aluminium based alloy solutions were prepared by dissolving on appropriate amount of the sample as described in chapter 3l and 3s.

A known aliquot amount of the alloy sample was treated with 4.0 ml of buffer solution (pH 9.0), 1.0 ml of 2-AAINH (1×10^{-2} M) and made up to the volume in a 10 ml volumetric flask with distilled water. The second order derivative curve was recorded and the derivative amplitudes were measured at 462 nm and 445 nm respectively. The amounts of Mn (II) and Ni (II) were computed from the measured amplitudes with the help of predetermined calibration plots. The results obtained are given in Table 8.iv.2.

Table 8.iv.2
Simultaneous determination of Mn (II) and Ni (II) in aluminum based alloys and alloy steel samples

Sample	Certified Value (%)		Amount found by Present method* (%)		Recovery (%)		Relative error (%)	
	Mn (II)	Ni (II)	Mn (II)	Ni (II)	Mn (II)	Ni (II)	Mn (II)	Ni (II)
BAS-20 ^a	0.19	1.93	0.191	1.929	100.52	99.94	+0.52	-0.05
BAS-85 ^b	0.02	0.91	0.0197	0.914	98.50	100.43	-1.5	+0.43
Alloy NTPC Ball bearing material ^c	2.0	10.0	2.02	10.03	101.00	100.30	+1.0	+0.30
Monel ^d	0.07	63.01	0.0698	63.05	99.71	100.06	-0.28	+0.06

Compositions (%)

a. Cu 4.10%; Ni 1.93%; Fe 0.43%; Mn 0.19%; Si 0.29%; Mg 1.61%; Rest

b. Cu 0.90%; Ni 0.91%; Fe 1.15%; Mn 0.02%; Si 2.04%; Mg 0.18%; Zn 0.01%; Rest Al

c. Fe 65%; Cr 15%; Cu 4.5%; Mn 2%; Ni 10%

d. Ni 63.01%; C 0.15%; S 0.002%; Mn 0.07% ; Si 0.05%; Fe 2.5%; Cu 31.0%

Section v : Simultaneous Second order derivative spectrophotometric determination of nickel (II) and cobalt (II)

In the present thesis to develop a simple and highly selective second order derivative spectrophotometric method for the simultaneous determination of nickel (II) and cobalt (II) in a mixture. Both of Ni (II) and Co (II) reacts with 2-Amino acetophenone isonicotinoyl hydrazone forming yellow and pink coloured water soluble complexes at pH 9.0 respectively. The second order derivative spectra of nickel and cobalt complexes were recorded in the wavelength region 400 – 600 nm and shown in Fig. 8.v.1. The second order derivative spectra of Ni (II) complex shows zero amplitude at 435 and 540 nm and considerably large amplitude at 450 nm with zero crossing at 465 nm. On the other hand, Co (II) complex with 2-AAINH shows sufficient amplitude at 540 nm (peak), 480 nm (valley) and zero amplitude at 450 nm with zero crossing at 520 nm. The experimental results indicate the derivative amplitudes obey Beer's law at 450 and 540 nm for Ni (II) and Co (II), respectively. The method has been applied for the simultaneous determination of nickel and cobalt in binary synthetic mixtures.

Experimental procedure

Different aliquots of solutions containing 0.2345- 1.5 $\mu\text{g mL}^{-1}$ of Ni (II) or 1.175-12.0 $\mu\text{g mL}^{-1}$ of Co (II) were transferred into a series of 10 ml standard flasks. 4ml of buffer solution (pH 9.0) and 1.0 ml of 2-AAINH (1×10^{-2}) were added to each of these flasks and diluted to the mark with distilled water. Second order derivative spectra were recorded for the two sets of solutions in the wavelength regions against reagent blank. Calibration plots were prepared by plotting the derivative amplitudes measured at 450 nm against the amount of nickel and the amplitudes measured at 540 nm against the amount of cobalt. The results obtained are shown in Table 8.iv.1.

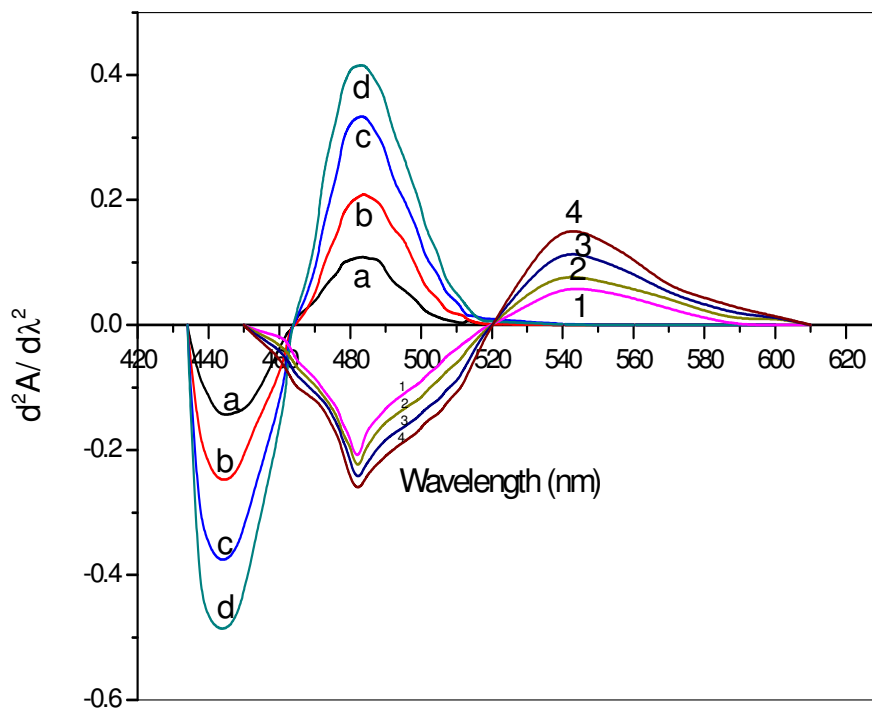


Fig. 8.v.1 : Second derivative spectra of [Ni(II)-2-AAINH], [Co(II)-2-AAINH] at different concentrations
 Ni(II) ($\mu\text{g mL}^{-1}$) = (a) 0.2342; (b) 0.4694; (c) 0.7041; (d) 0.9888
 Co(II) ($\mu\text{g mL}^{-1}$) = (1) 1.176; (2) 2.356; (3) 4.712; (4) 7.056

Verification of Beer's law validity

Individual Beer's law plots were constructed for Ni (II) and Co (II) complexes by measuring the second derivative amplitudes for variable amounts of Ni (II) at 450 nm and Co (II) at 540 nm. The plots were shown in Figs. 8.v.2 and 8.v.3 for Ni (II) and Co (II) respectively. The Beer's law was obeyed in the range of 0.06–3.0 $\mu\text{g mL}^{-1}$ of Ni (II) and 0.04–3.5 $\mu\text{g mL}^{-1}$ of Co (II).

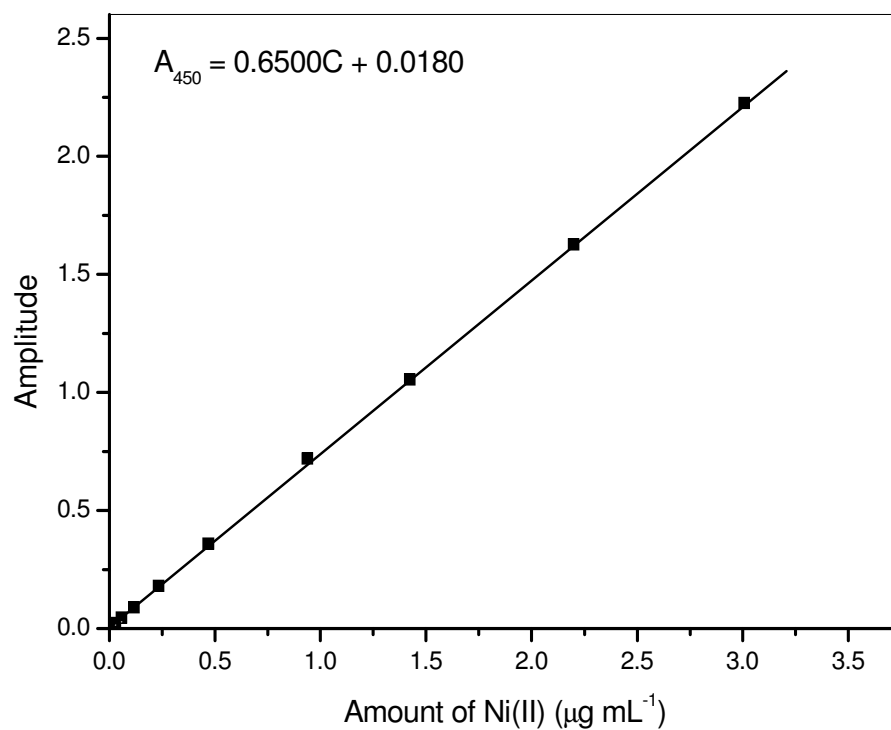


Fig. 8.v.2. : Second derivative amplitude Vs amount of Ni(II)
 $[2\text{-AAINH}] = 8 \times 10^{-4} \text{ M}$
 $\lambda = 450 \text{ nm}$; $\text{pH} = 9.0$

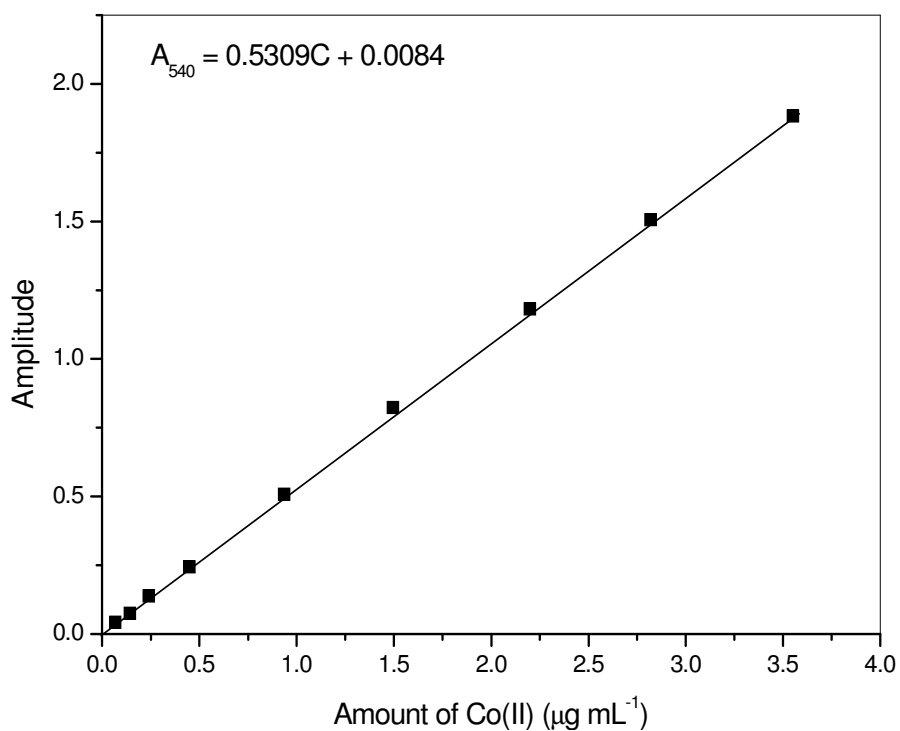


Fig. 8.v.3. : Second derivative amplitude Vs amount of Co(II)
 $[2\text{-AAINH}] = 8 \times 10^{-4} \text{ M}$
 $\lambda = 450 \text{ nm}$; $\text{pH} = 9.0$

Table 8.v.1**Simultaneous Second order derivative determination of Ni (II) and Co (II)**

Amount taken ($\mu\text{g mL}^{-1}$)		Amount found* ($\mu\text{g mL}^{-1}$)		Recovery (%)	
Ni (II)	Co (II)	Ni (II)	Co (II)	Ni (II)	Co (II)
0.2342	1.176	0.2340	1.172	99.91	99.65
0.2342	1.176	0.2343	1.175	100.04	99.91
0.2342	1.176	0.2339	1.179	99.87	100.25
0.4694	2.356	0.4697	2.350	100.06	99.74
0.7041	2.356	0.7044	2.360	100.04	100.16
0.9888	4.712	0.9893	4.716	100.05	100.08

* Average of five determinations.

Applications

The present simultaneous method was employed for the determination of amounts of Ni (II) and Co (II) in Eligiloy M-1712, BCS 406/1, alloy steels and soil samples. The steel and soil samples were brought into solution by employing the general procedure described in chapter 3l and 3q.

A known aliquot of the steel sample was treated with 4.0 ml of buffer solution (pH 9.0), 1.0 ml of 2-AAINH ($1 \times 10^{-2}\text{M}$) and made up to the mark in a 10 ml volumetric flask with distilled water. The second derivative curve was recorded and the derivative amplitudes were measured at 450 nm and 540 nm. The amounts of nickel and cobalt were computed from the measured amplitudes with the help of predetermined calibration plots. The results obtained are given in table 8.v.2.

Table 8.v.2**Simultaneous determination of Ni (II) and Co (II) in alloy steel samples**

Sample	Certified Value (%)		Amount found by Present method* (%)		Recovery (%)		Relative error (%)	
	Ni (II)	Co (II)	Ni (II)	Co (II)	Ni (II)	Co (II)	Ni (II)	Co (II)
Eligiloy M-1712 ^a	15.00	40.00	14.95	40.06	99.66	100.15	-0.33	+0.15
BCS 406/1 ^b	0.14	0.016	0.142	0.0157	101.42	98.12	+1.42	-1.8
Alloy steel ^c	11.22	23.72	11.26	23.68	100.35	99.83	+0.35	-0.16

* Average of five determinations;

a = Cr 20%; Co40%; Ni 15%; C0.15%; Fe15%; Mn2%; Mo7%; Be0.05%.

b = Mn 0.066%; Cr1.06%; Mo0.05%; Ni0.14%; Co0.016%; Cu0.091%; V0.19%.

c = Fe51.15%; Ni11.22%; Cu5.09%; Co23.72%; Al6.98%; Ti0.79%; Mn0.235%; Si0.57%.

Application to Soil sample

Soil sample (S-18) supplied by Geological Survey of India (GSI), Bangalore was analyzed and the amounts of nickel and Cobalt present in the sample were simultaneously determined by the present method. The results were compared with those provided by G.S.I. and presented in table 8.v.3.

Table 8.v.3**Analysis of Soil sample**

Sample and composition ($\mu\text{g mL}^{-1}$)	Certified(GSI) value ($\mu\text{g mL}^{-1}$)		Amount found by Present method* ($\mu\text{g mL}^{-1}$)		Recovery (%)		Relative error (%)	
	Ni (II)	Co (II)	Ni (II)	Co (II)	Ni (II)	Co (II)	Ni (II)	Co (II)
S-18 20.20 Pb (II); 20.30 Zn (II); 88.85 Cu (II)	50.50	40.35	50.74	40.05	100.47	99.25	+0.47	-0.74

* Average of five determinations

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