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RESEARCH ARTICLE

Simultaneous Fourth Order Derivative Spectrophotometric Determination of Cobalt, Nickel and Copper Using Anthrone Phenylhydrazone (APH)

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Abstract: The reagent anthrone phenylhydrazone (APH) is used for the simultaneous determination of Co(II), Ni(II) & Cu(II) by fourth order derivative spectrophotometric method. The reagent APH gives light yellow colour with Co(II), Ni(II) & Cu(II) solution in basic medium. The maximum peaks were observed between 426.3-625 nm for Co(II), Ni(II) & Cu(II) in basic buffer solution of pH 10. The molar absorptivity and Sandell`s sensitivity of Co(II), Ni(II) & Cu(II)-APH complexes are computed, the molar absorptivity are $1.5x10^4$ L/mol/cm, $2.0x10^4$ L/mol/cm and $2.163x10^4$L/mol/cm respectively. The Sandell`s sensitivity are 0.0066 µg/cm^2, 0.005 µg/cm^2 and 0.0026 µg/cm^2 respectively. The stability constant of Co(II), Ni(II) & Cu(II)-APH complexes are $1.530x10^5$, $2.486x10^4$ and $2.96x10^4$ respectively. The effect of various concentrations of Co(II), Ni(II) & Cu(II) ions on amplitude also studied. The samples of grape leaves, sesame, laver, mung bean and alloy samples were analyzed by the proposed method. The results of the food samples and alloy samples are good agreement with the results of APARI, AAS methods.

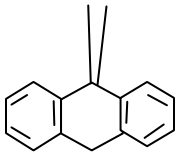
Keywords: APH, Simultaneous spectrophotometry, Cobalt(II), Nickel(II), Copper(II)

Introduction

Anothrones are known as carcinogenic compounds. Anthrone derivatives are found to have biological activity[1]. These compounds have an azomethine nitrogen atom and this is responsible for their reactivity with a number of transition metal ions which form colored complexes. Its derivatives such as anthralin and anthraquinone, their functions were studied with the inner mitochondrial membrane. Anthralin readily oxidizes to anthralin dimer and anthraquinone; these compounds have also been identified as skin metabolites[2-4]. Solubilities of some 9-anthrone derivatives and aminoanthraquinone derivatives in supercritical carbon dioxide were studied using a simple and reliable static method[5-6]. Anthranoid laxatives are the most commonly used purgatives in the therapy of acute and chronic constipation[7-8]. Further the metal complexes formed with these reagents are of great medicinal value in the treatment of diseases like colorectal cancer, psoriasis, chronic constipation, tumor related problems regarding[9-16]. In this article, the authors present fourth derivative spectrophotometric method for the simultaneous determination of cobalt, nickel and copper.

Experimental

The reagent anthrone phenylhydrazone was prepared by simple condensation of anthrone with phenyhydrazine by adopting the standard procedure. The structure of compound is given below, $NNHC_6H_5$ [Anthrone phenylhydrazone (APH)].



The structure has been established based on IR, mass and NMR spectra. The m.p. of APH is 145-149 ^{0}C.

Solutions preparation

Buffer solutions are prepared using HCl, CH_3COOH and NaOAC in acidic medium and NH_4OH, NH_4Cl in basic medium.

Preparation of metal and reagent solutions

The standard Co(II), Ni(II) and Cu(II) solutions were prepared using analytical reagent grade $CoCl_2.6H_2O$, $NiCl_2.6H_2O$ and $CuSO_4.2H_2O$. Appropriate quantity of APH is dissolved in DMF for making 0.01 M reagent solution.

Procedure

Preparation of standard derivative spectrum

4 mL of basic buffer solution of pH 10, varying concentrations of each of the metal solutions of Co(II), Ni(II) and Cu(II), 6 mL of 10^{-3} M of APH are taken in a 25 mL volumetric flask, the contents are made up to the mark with double distilled water and the amplitudes of these solutions were measured between 350-750 nm against reagent blank.

Shimdzu 160A UV-visible spectrophotometer (Japan) equipped with 1 cm quartz cell was used in these investigations for making amplitude measurements. A pH meter ELICO L_1-120 (Hyderabad) is used to make pH measurements.

Preparation and analysis of samples

Food samples or alloy samples were weighed accurately and digested with nitric acid and perchloric acid for determination of Co, Ni and Cu. The residue was dissolved with 10 mL double distilled water for determination. 3 mL of the digested sample solution, 4 mL of basic buffer solution of pH 10 and 6 mL of APH reagent were taken into a 25 mL volumetric flask. The derivative spectra of analytes in the sample were recorded using the same procedure. According to the concentrations and amplitudes of standard solutions, the contents of the sample can be calculated from derivative spectrum obtained from sample.

Results and Discussion

Derivative spectra of Co, Ni and Cu complexes

The zero order spectrum of a mixture containing cobalt, nickel and copper in presence of APH gives only one peak, no resolution takes place and hence simultaneous determination is not possible and is shown in Figure 1. Hence we have made an attempt to use first, second and third order derivative spectra but, no fruitful results obtained. Finally we have made an attempt to use a 4^{th} order derivative spectrum for possible simultaneous determination of the three metal ions and it is shown in Figure 2.

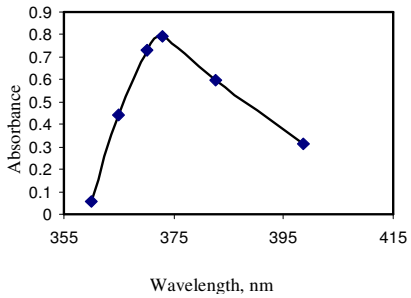


Figure 1. Zero order spectrum of Co(II)+Ni(II)+Cu(II) in presence of APH. *[Co(II)] = [Ni(II)] = [Cu(II)] 1x10^{-5} M; [APH]= 2.4x10^{-4} M, pH = 10*

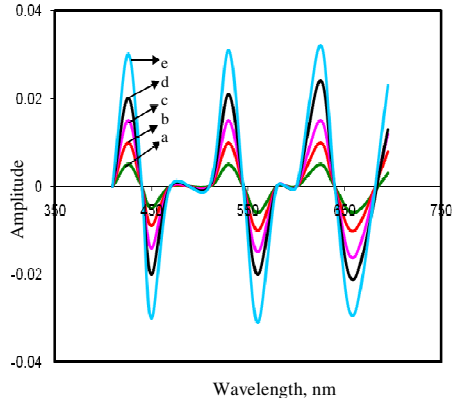


Figure 2. 4th Order derivative spectrum of Co(II)+Ni(II)+Cu(II) in presence of APH *[Co(II)] = [Ni(II)]=[Cu(II)]=1x10^{-5} M, [APH] =2.4x10^{-4} M, pH=10; a) 0.5 mL of Co(II), Ni(II) and Cu(II) each, b) 1.0 mL of Co(II), Ni(II) and Cu(II) each, c)1.5 mL of Co(II), Ni(II) and Cu(II) each, d) 2.0 mL of Co(II), Ni(II) and Cu(II) each, e) 2.5 mL of Co(II), Ni(II) and Cu(II) each*

The 4th order derivative spectra are recorded in one case keeping Co(II) constant and varying both Ni(II) & Cu(II) concentration and is shown in Figure 3. In the second case the Ni(II) concentration is kept constant and both Co(II) & Cu(II) concentrations are varied shown in Figure 4. In the third case the Cu(II) concentration is kept constant and both Ni(II) & Co(II) concentrations are varied shown in Figure 5.

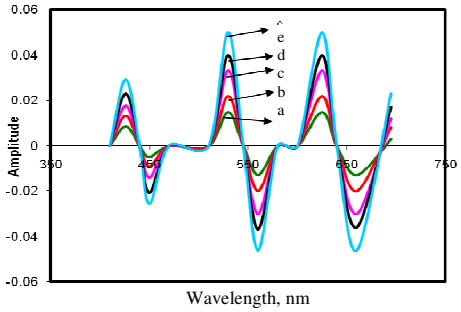


Figure 3. 4th order derivative spectrum of Co(II)+Ni(II)+Cu(II) in presence of APH. *Cobalt concentration is kept constant by varying concentration of both Ni^{2+} and Cu^{2+}. [Co(II)] = [Ni(II)] = [Cu(II)] = 1x10^{-5} M, [APH] =2.4x10^{-4} M, pH=10; a) 0.5 mL of Co(II), 1.0 mL of Ni(II) and 1.0 mL of Cu(II); b) 1.0 mL of Co(II), 1.5 mL of Ni(II) and 1.5 mL of Cu(II); c) 1.5 mL of Co(II), 2.0 mL of Ni(II) and 2.0 mL of Cu(II); d) 2.0 mL of Co(II), 2.5 mL of Ni(II) and 2.5 mL of Cu(II); e) 2.5 mL of Co(II), 3.0 mL of Ni(II) and 3.0 mL of Cu(II)*

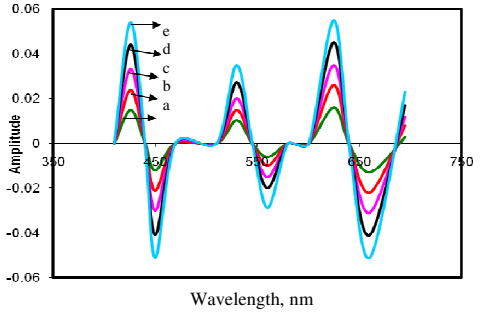


Figure 4. 4th order derivative spectrum of Co(II)+Ni(II)+Cu(II) in presence of APH. *Nickel concentration is kept constant by varying concentration of both Co^{2+} and Cu^{2+}. [Co(II)] = [Ni(II)] = [Cu(II)] = 1x10^{-5} M, [APH] =2.4x10^{-4} M, pH=10; a) 1.0 mL of Co(II), 0.5 mL of Ni(II) and 1.0 mL of Cu(II); b) 1.5 mL of Co(II), 1.0 mL of Ni(II) and 1.5 mL of Cu(II); c) 2.0 mL of Co(II), 1.5 mL of Ni(II) and 2.0 mL of Cu(II); d) 2.5 mL of Co(II), 2.0 mL of Ni(II) and 2.5 mL of Cu(II); e) 3.0 mL of Co(II), 2.5 mL of Ni(II) and 3.0 mL of Cu(II)*

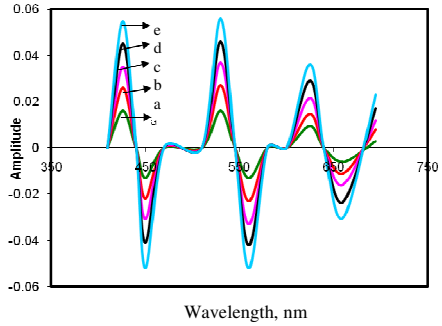


Figure 5. 4th order derivative spectrum of Co(II)+Ni(II)+Cu(II) in presence of APH.

Copper concentration is kept constant by varying concentration of both Ni^{2+} and Co^{2+}. [Co(II)] = [Ni(II)] = [Cu(II)] = $1x10^{-5}$ M, [APH] =$2.4x10^{-4}$ M, pH=10; a) 1.0 mL of Co(II), 1.0 mL of Ni(II) and 0.5 mL of Cu(II); b) 1.5 mL of Co(II), 1.5 mL of Ni(II) and 1.0 mL of Cu(II); c) 2.0 mL of Co(II), 2.0 mL of Ni(II) and 1.5 mL of Cu(II); d) 2.5 mL of Co(II), 2.5 mL of Ni(II) and 2.0 mL of Cu(II); e) 3.0 mL of Co(II), 3.0 mL of Ni(II) and 2.5 mL of Cu(II)

Graphs are drawn between Co(II) concentration against peak amplitude, Ni(II) concentration against peak amplitude and Cu(II) concentration against peak amplitude. Linear graphs are obtained in all the three cases and shown in the Figures 6, 7 and 8. Hence using the fourth order derivative spectrophotometric method, we can determine Co in presence of Ni and Cu and *vice-versa*.

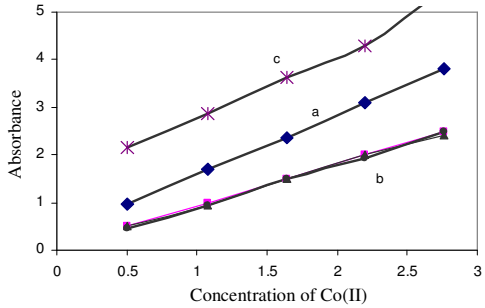


Figure 6. 4th order derivative amplitude *vs.* concentration of Co(II) pH=10, a=peak; b=valley; c=peak+valley

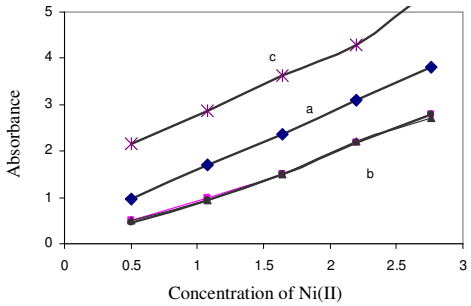


Figure 7. 4th order derivative amplitude *vs.* concentration of Ni(II) pH=10, a=peak; b=valley; c=peak + valley

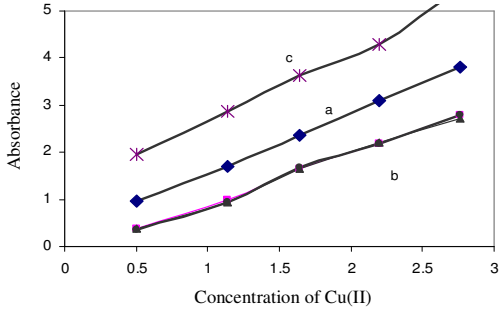


Figure 8. 4th order derivative amplitude *vs.* concentration of Cu(II) pH=10, a=peak; b=valley; c=peak + valley

Influence of the variables

APH is a kind of high sensitive carcinogenic reagent and it can form colored complexes with many transition metals in neutral and basic medium. The experiments are carried out in the pH range 7- 12. The results showed that the absorbances of three complexes were highest and the complexes are stable in the pH range 10-11. The effect of pH on the absorbances are shown in the Figures-9, 10 and 11. Further Co(II), Ni(II) and Cu(II) do not form stable complexes in acidic medium. It may be due to the hydrolysis of the reagent or the complex itself. In highly alkaline medium (>pH11) slow turbidity develops which may be due to formation of hydroxides. Studies relating to the effect of time revealed that the complex is stable for a considerable amount of time.

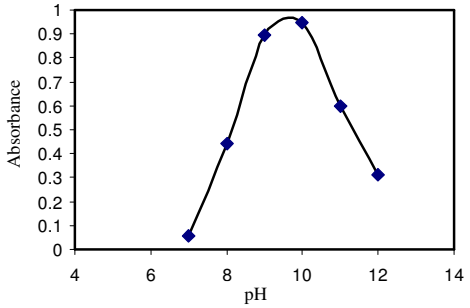


Figure 9. Effect of pH on the absorbance of cobalt (II)-APH system [Cobalt(II)]=3x10^{-5} M, [APH] =2x10^{-4} M

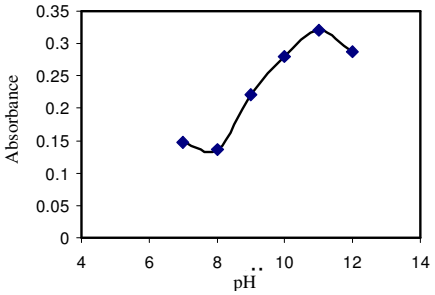


Figure 10. Effect of pH on the absorbance of nickel (II)-APH system [Nickel(II)] =3x10^{-5} M, [APH] =2x10^{-4} M

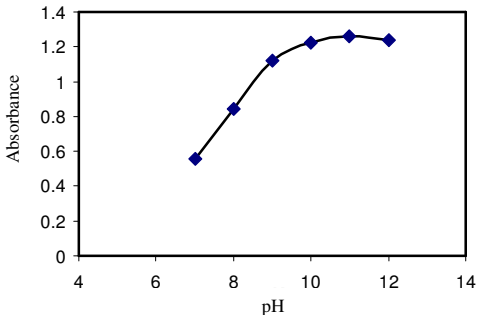


Figure 11. Effect of pH on the absorbance of copper(II)-APH system [Copper(II)] =3x10^{-5} M, [APH] =2x10^{-4} M

The effect of metal ion concentrations (4x10^{-5} M) on absorbances is studied by keeping the reagent concentration constant (2.4x10^{-4} M). The absorbance values are measured at 373, 364 and 370 nm for cobalt, nickel and copper respectively against suitable blank solution containing no metal ion. Linear plots are obtained in all the three cases when graphs are plotted between the metal ion concentration and absorbance and are presented in the Figures-12, 13 and 14. The determination limits were 0.201-1.807, 0.411-4.811 and 0.402-1.810 µg/mL for cobalt, nickel and copper respectively. The stoichiometry of these three metal ions with APH was studied by Job`s method of continuous variation and also the mole ratio method. Both the methods indicated the formation of a 1:1.4, 1:2 and 1:1 complex for cobalt, nickel and copper respectively. By knowing this stoichiometry a 35 fold concentration of APH is taken to react with the three metal ions.

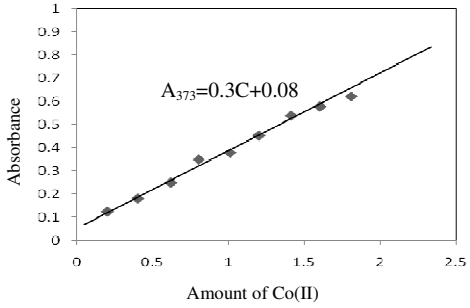


Figure 12. Effect of metal ion concentration on absorbance λ_{max}=373 nm, [Co(II)] =4x10^{-5} M, [APH]=2.4x10^{-4} M, pH=10

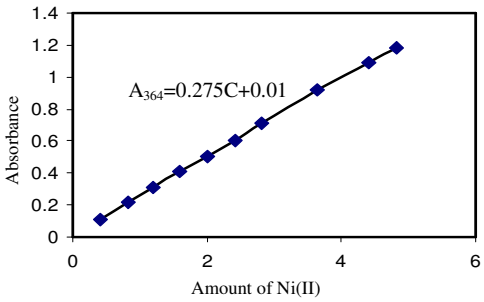


Figure 13. Effect of metal ion concentration on absorbance λ_{max}=364 nm, [Ni(II)] =4x10^{-5} M, [APH] =2.4x10^{-4} M, pH=11

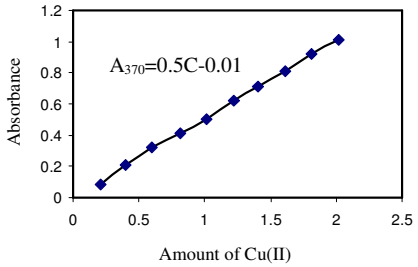


Figure 14. Effect of metal ion concentration on absorbance λ_{max}=370 nm, [Cu(II)] =4x10^{-5} M, [APH]=2.4x10^{-4} M, pH=10.5

The stability constants of Co(II), Ni(II) & Cu(II)-APH complexes were calculated from Job`s method. They are found as 1.530x10^{5}, 2.486x10^{4} and 2.96x10^{4} for Co(II), Ni(II) and Cu(II) respectively. The effect of interfering species of 23 metal ions commonly found in food samples is investigated. The most interfering ions tested did not interfere in the determination and shown in Table 1.

Table 1. Tolerance limit of foreign ions. Tolerance limit of foreign ions in the determination of 0.841 µg/mL of Co(II), 1.35 µg/mL of Ni (II) and 0.94 µg/mL of Cu(II) pH = 10 λ_{max} = 364 nm

Foreign ion	Tolerance limit, µg/mL	Foreign ion	Tolerance
Thiourea	94	Mn(IV)	2.54
Tartrate	319	U(VI)	96.21
Sulfate	755	Ru(III)	13.20
Phosphate	163	Se(IV)	116
Fluoride	17	Pb(II)	2.53
Chloride	44.21	Cd(II)	3.84
Iodide	63.8	Zr(IV)	3.73
Nitrate	112.23	Ti(IV)	123.18
Oxalate	16.57	Sn(II)	2.27
EDTA	316.4	Mg(II)	1.55
Thiosulfate	55.23	Zn(II)	1.74
Bromide	440	W(VI)	745.4
Citrate	841	Pd(II)	0.55
Acetate	144.3	Hg(II)	11.19
		Fe(II)	2.65
		Mo(VI)	66.25

Application

The present method is applied for the determination of three metal ions simultaneously in sesame, laver, soyabean powder and alloy samples. The repeatability and precision of the method were satisfied with RSD in the range of 0.0563-0.0888% for five determinations. Therefore, the three metal ions can be directly determined after digestion without any pretreatment by the proposed method. Accuracy of the proposed method was validated using a certified reference material of tea and grape leaves (GBW07605 and GBW08501, Chinese Standard material center) (AAS and APARI, Hyderabad). The values determined by the proposed method and the determined values (n=5) of the certified reference material were within the given guarantee values and shown in the Table 2.

Table 2. Analysis of alloy samples

Sample	ASTM method, %			By Present method, %			% Error		
	Co(II)	Ni(II)	Cu(II)	Co(II)	Ni(II)	Cu(II)	Co(II)	Ni(II)	Cu(II)
Co-Cr alloy	62.9	1.7	0.9	62.1	1.9	0.7	+1.271	-11.76	+11.76
Ni-Cr-Mo alloy	50.6	14.9	1.5	50.9	14.6	1.7	-0.592	+2.013	-1.333
Ground nut seeds	1.175 µg/mL	4.205 µg/mL	1.248 µg/mL	1.189 µg/mL	4.198	1.240	-1.191	+0.166	+0.641

Conclusion

In this article, a multi-component analysis with 4th order derivative spectrophotometry has been developed. The proposed method has been successfully applied for the simultaneous determination of Co, Ni and Cu in certified reference materials and food samples after digestion without further pretreatment. Compared with the traditional spectrophotometry, the proposed method provides good results for three analytes in terms of accuracy and precision and allows 44 determinations per hour for the digested food samples and the results proved to be satisfactory and meet the criterion of food analysis.

References

1. Hedge J E and Hofreiter B T, In Carbohydrate Chemistry, 17 Academic Press, New York, 1962.
2. Whistler R L and Be Miller J N, Eds., Methods in Carbohydrate Chemistry, 1962.
3. Thayumanavan B and Sadasivam S, *Qual Plant Foods Hum Nutr*., 1984, **34**, 253.
4. Updegroff D M, *Anal Biochem*., 1969, **32,** 420-424.
5. Ali Reza Karami**,** Yadollah Yamini**,** Ali Reza Ghiasvand, Hashem Sharghi and Mojtaba Shamsipur, *J Chem Eng Data*, 2001**, 46(6)**, 1371-1374.
6. Mojtaba Shamsipur**,** Ali Reza Karami, Yadollah Yamini and Hashem Sharghi, *J Chem Eng Data,* 2003, **48(1)**, 71–74.
7. Kune G A, Kune S, Field B and Watson L F, *Dis Colon Rectum*., 1988; **31**, 507–512.
8. Nusko G, Schneider B, Ernst H, Wittekind C and Hahn E G, *Gastroenterol.,* 1997, **35,** 313-318.
9. Patel P M, Selby P J, Deacon J, Chilvers C and McElwain T J, *Postgrad Med J.,* 1989, **65**, 216-17.
10. Siegers C P, Hertzberg-Lottin Evon, Otte M and Schneider B*, Gut.,* 1993, **34,** 1099–1101.

11. Jass J R and Sobin L H, Histological Typing of Intestinal Tumours, WHO International Classification of Tumours, 2nd Edn., Berlin: Springer, 1989.
12. Breslow N E and Day N E, Statistical Methods in Cancer Research, Vol. I -The analysis of case control studies, Lyon: IARC, 1980**.**
13. Parkin D M, Läärä E and Muir C S, *Int J Cancer*, 1988, **41,**184-197.
14. Thun M J, Calle E E and Namoodiri M M, *et al*., *J Natl Cancer Inst.*, 1992, **84,** 1491-1500.
15. Boeing H and Wahrendorf J, Internist (Berl), 1991, **32(6),** 306-314.
16. Thipyapong K and Suksai C, *Bull Korean Chem Soc.*, 2003, **24(12)**, 1767–1770.