



Research Article

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Novel simultaneous spectrophotometric determinations of Bi (III), Sn (II), Mn (II), V (III) and Se (II) ions in mixed aqueous solutions

*Ekere N. R., Okoye C. O. B. and Ihedioha J. N.

Analytical/Environmental Chemistry Laboratory, Department of Pure & Industrial Chemistry University of Nigeria, Nsukka, Enugu State, Nigeria

ABSTRACT

This paper reports a novel simultaneous uv-vis spectrophotometric determination of Bi (III), Sn (II), Mn (II), V (III) and Se (II) in mixed aqueous solution using 3,3',4',5,7 – pentahydroxy flavuylium (cyanidin) as complexing agent. The maximum absorption wavelengths (λ_{max}) of Bi – cyanidin; Sn – cyanidin; Mn – cyanidin, V – cyanidin and Se – cyanidin complexes were 277 nm, 232 nm, 240 nm, 272 nm and 251 nm respectively as against that of pure cyanidin which was 280 nm at the determined optimal pH value of 5. Spectral overlap did not occur among the metal complexes and linearity occurred with the range of 0.50 ppm to 2.5 ppm. This method has potentials for a simple, cheap, rapid and eco-friendly way of trace heavy metals determinations in biological and environmental samples.

Key words: Spectrophotometry; trace metals; cyanidin, aqueous, bismuth (III), vanadium (III) selenium (II), complexes.

INTRODUCTION

Determination of trace heavy metals present in the environment has been given prominence due to the toxicity of some of them to man and the environment. Several methods have been developed for their simultaneous determination in environmental, food, drugs and biological samples. Among these techniques are adsorptive stripping voltammetry [1, 2], atomic absorption spectroscopy [3] and chromatography [4]. Other methods offering simultaneous determination in mixed aqueous solutions as well as in environmental, industrial and biological samples are plasma based techniques such as inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and inductively coupled plasma-mass spectroscopy (ICP-MS) [5]. Among these methods, atomic absorption spectroscopy (AAS) is the most common. All these methods produce robust results and are quite sensitive and fast but their major setbacks are prohibitive cost of the instruments, sophistication of technical know-how, running and maintenance cost and high cost of chemicals and reagents. There are also environmental concerns such as release of mercury vapour into the air during AAS determination. Ultra violet – visible (uv-vis) spectroscopy is a traditional and widely used technique for single element determination of metal ions in solutions [5,6,7]. Some workers have achieved simultaneous analysis of metals using various complexometric methods with uv-vis spectroscopy [4,5,8,9]. Most of these ligands are not environmentally friendly [10].

The use of flavonoids as analytical reagents have been reported, based in their abilities to form complexes with some p, d and f-electron metals and the complexes formed make the basis of determination of metals by uv-vis spectrophotometry and spectrofluorimetry. Morin and Quercetin have been used in determination of A (III) [5], Cr

(III) and W (IV) [6], Ge (IV) [7]. However, Okoye et al [12,13] have applied complexation with cyanidin in a simple, sensitive cheap and environmentally friendly multi-element metal determination using uv-vis spectroscopy.

This paper presents a study of simultaneous determination of some heavy toxic metals in mixed aqueous solutions using cyanidin as the metallochromic agents. The method, being simple, rapid, and cheap is attractive and has potentials for use in environmental, food, drug and biological samples.

EXPERIMENTAL SECTION

2.1 Equipment and Chemicals

Absorption measurements were made using UV-2102 PC Spectrophotometer UNICO®. pH measurements were carried out with JenWay (3015 – model) pH meter.

All the chemicals used were of analytical grade supplied by Rie-del Haem, Germany. Stock solutions of the metals ions were prepared from chlorides for Sn (II) and Mn (II); oxides for Bi (III) and V (III) and Se powders.

2.2 Extraction of cyanidin

Cyanidin in was extracted from dried calyces of Roselle plant (*Hibiscus Sabdarifa. L*), harvested from botanical garden, University of Nigeria, Nsukka and was certified as authentic sample by experts from Plant Science and Biotechnology Department of the University. A 500 g weight of the calyces was ground to powder using a stainless grinding machine and macerated in 2 L (85:15 v/v) methanol/ 2M HCl mixture for 72 h and filtered. The filtrate was concentrated to 500 ml. A volume of 100 ml of concentrated HCl was added and the mixture refluxed for 2 h. The resulting solution was transferred into a beaker, covered and cooled in a refrigerator until crystals settled out. The crystals were filtered under suction, re-crystallized from hot methanol, dried and weighed. The result of the analysis of the crystals conformed to all the analytical data earlier published earlier [11,12,13].

2.3 Preparation of standard solutions.

All metallic salts, oxides and metal used for preparation of stock solutions were heated in an oven at a temperature of 105 -110°C for 1 h to drive out moisture.

Bismuth (III) oxide (0.11 g) was dissolved in 50 ml of deionized water in a beaker and transferred into a 1000 ml standard flask and made up the mark to give 100 ppm standard solution. Anhydrous stannous chloride (0.16 g) was dissolved in 50 ml of the deionized water in a beaker and transferred into a 1000 ml standard flask and made up the mark to prepare 100 ppm standard tin (II) solution. Also, 0.23 g of manganese (II) chloride was dissolved in 50 ml of deionized water, transferred into a 1000 ml standard flask and made up the mark to produce 100 ppm standard solution of manganese (II). Anhydrous vanadium (III) oxide (0.15 g) was dissolved in 50 ml of deionized water, transferred into 1000 ml standard and made up the mark to prepare 100 ppm stock solution of vanadium (III). Selenium powder (0.10 g) was dissolved in 50 ml of deionized water in a beaker, transferred into a 1000 ml standard volumetric flask and the volume made up to give a 100 ppm Selenium standard solution. All the solutions prepared were each serially diluted to 0.5; 1.0, 1.5, 2.0 and 2.5 ppm working standard solutions.

2.4 Determination of wavelength of maximum absorption (λ_{max}) and optimal pH (pH opt.) of the metal cyanidin complexes.

One percent (1%) cyanidin solution was prepared by dissolving 1 g of cyanidin in small quantity of methanol, transferred to a 100 ml volumetric flask and the mark made up with methanol. For each metal-cyanidin complex, 5 ml of the 100 ppm stock solution was added to 5 ml of 1% cyanidin in methanol and the wavelength of absorption scanned from 200 nm to 700 nm to obtain the λ_{max} . Also, the wavelength of absorption of pure cyanidin solution was scanned and its λ_{max} read.

Buffer solutions of pH ranges 1 to 8 were prepared as prescribed [15, 16]. 5 ml of each metal solution was put into eight bottles containing 5 ml of 1% cyanidin in methanol and the pH of each cyanidin complex adjusted between 1 and 8. The absorbance of each complex at specific pH was taken. This process was carried out for all the five metal-cyanidin complexes.

2.5 Simultaneous determination of the metals

A 2.5 ml portion of each metal stock solution was mixed in a 250 ml standard flask and the mark made up with deionized water to produce a 5 ppm mixed standard solution. The mixed standard solution was serially diluted to provide 0.5, 1.0, 1.5, 2.0, 2.5 ppm working standards. 5 ml portion of the mixed standard solution of each working standard was mixed with 5 ml of 1% cyanidin solution in a sample bottle and the pH adjusted to the determined optimal pH (pH=5) and the absorbencies recorded at the λ_{max} of each metal –cyanidin complex. The procedure was repeated for all the determined concentrations.

RESULT AND DISCUSSION

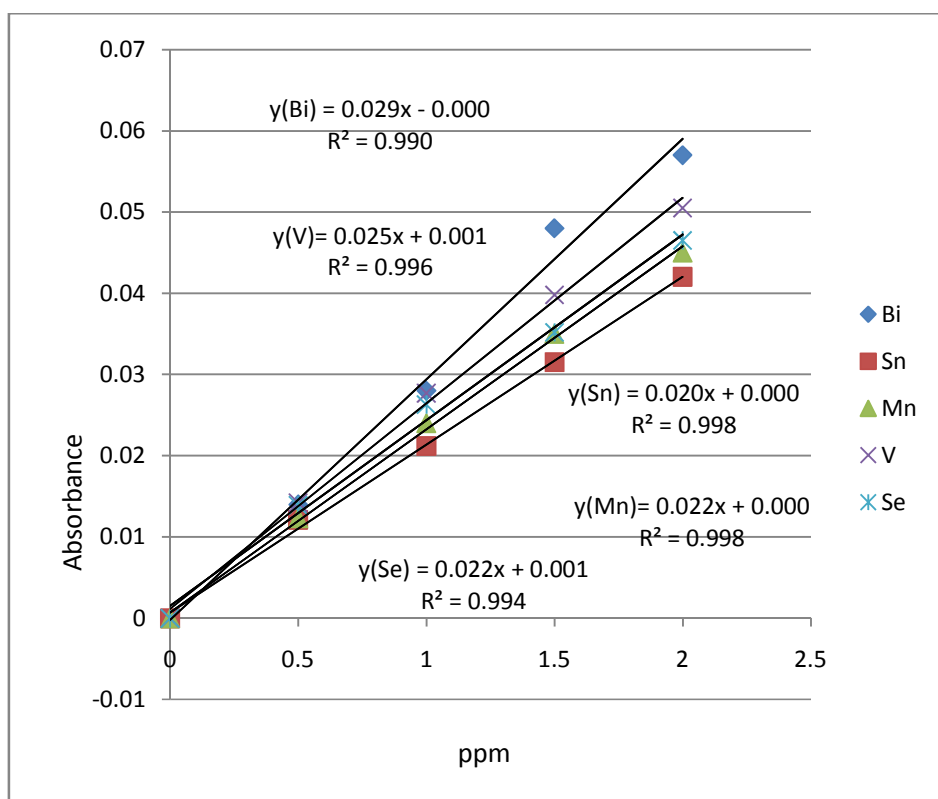
The R_f values and uv-vis spectral data of cyanidin conformed with the existing literature [11, 12, 13]. Hence the crystals from *Hibiscus sabdarifa* L flowers were actually 3,3',4',5',7 – pentahydroxy flavylium ion (cyanidin). Complexation of cyanidin with the metals ions produced blue shift in the absorption wavelength of cyanidin as shown in Table I.

Table I. Maximum wavelength (λ_{max}) of metal –cyanidin complexes

Substance	Cyanidin	Bi –Cy	Sn – Cy	Mn –Cy	V – Cy	Se – Cy
λ_{max} (nm)	282	277	232	240	272	251

Cy = Cyanidin

Figure I. Mixed graph of absorbance against concentration of the metal –cyanidin complexes



Investigations into the effects of pH on the complexation show that the optimal pH for the reactions is 5 which is in agreement with earlier similar work by the researchers [12,13]. As a result, all the studies were carried out at the optimal pH. The metal-cyanidin complexes did not absorb in the visible region.

It has been reported that all flavonoids possess three domains capable of reacting with metal ions [17]. The domains are the 3', 4' dihydroxy system; the 3-hydroxy or 5-hydroxy groups and 4-carbonyl group. Earlier study by

Ukwueze and co-workers [14] showed that cyanidin – metal complex formation is in the ratio of 1:2 and occurred at the 3¹, 4¹ –dihydroxy domain of the ligand. Merlin and Cornard [17] reported that in acidic conditions, 1:1 ratio between metal and quercetin was favoured in complex formation. The use of methanol as the solvent system promoted 1: ratio between metal and ligand. [18]

The linearity of calibration curves of the metal ions complexes over a concentration range of 0.0 to 2.5ppm was studied. The metal – cyanidin complexes obeyed Beer-Lambert's law over the studied concentration range at the optimal pH value. The calibration curves were shown in Figure I.

As shown in the figure, the linear regression equations and R² values indicated that these metal ions can be simultaneously determined with confidence at the concentration range. However,, these is interference among the metal-cyanidin complexes at low concentrations of $\leq 0.5\text{ppm}$.

CONCLUSION

This uv –vis spectrophotometric method for simultaneous determination of heavy metals offers a simple, rapid cost effective and environmental friendly technique. The method has potential of usage in determination of heavy metals in food, drugs and environmental samples.

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