A CATALYTIC METHOD FOR THE DETERMINATION OF TRACE AMOUNTS OF MERCURY UPTAKEN BY BROAD BEANS PLANTS

Bassem F. Shraydeh[1]* , Maher Abu-Eid[1], Nidal A. Zatar[1],
Ismat Shakhshier[1] and Mustafa Khamis[2]
[1] Chemistry Department, An-Najah N. University, Nablus, West Bank, Via Israel
[2] College of Science and Technology, Abu-Dis, West Bank, Via Israel

Abstract

A new accurate, fast catalytic method for the determination of trace amounts of mercury uptaken by plants is proposed. The method is based on the catalytic effect of mercury(II) on the rate of ligand-exchange reaction between ferrozine and hexacyanoferrate(II) whereby a coloured violet complex is formed which absorbs at 562 nm. The method allows the determination of mercury(II) in the range 0.05-4.0 ppm. The effect of pH, hexacyanoferrate, ferrozine, temperature, time of reaction and tolerance limit of many ions have been reported. The method is applied to the determination of mercury(II) uptaken by broad beans plants irrigated with water containing different amounts of mercury(II).

Introduction

It was observed that mercury(II) catalyses the reaction between ferrozine $K_4Fe(CN)_6$ to give a stable violet complex that absorbs at 562 nm. Hence this reaction was utilized for developing a new catalytic method for the determination of mercury(II) uptaken by broad beans plants.

Experimental

Reagents:

All reagents used were of analytical-reagent grade and 1×10^{2} M stock solution were prepared from these reagents. In each case, working solutions were prepared by appropriate dilution. The buffer solutions were acetic acid-sodium acetate mixture for pH in the range 2.0-6.0 and boric acid-sodium tetraborate mixtures for pH in the range 6.5-8.0.

Apparatus:

A Perkin-Elmer Lambda 5 double beam spectrophotometer with 1 cm quartz cell and constant temperature cell holder was used for recording spectra and absorbance-time curves.

Plant: Three good seeds of broad beans were planted in each plastic pot, under green house conditions. Each pot was filled with 3.5 kg mixture of brown soil and sand (2:1 V/V).

General Procedure

Chemical Analysis of Plants:

The completely grown plants were cut into roots, stems, leaves and fruits. Each part was then cleaned thoroughly with distilled water. 15 g of each part of the plant were treated with 25 g of 62% HNO_3 and digested for 2 hours. After that the solution was filtered through filter paper. The residue was washed in the filter 2-3 times with 3-5 ml portions of distilled water. The solution was evaporated and the volume was adjusted to 10 ml and analyzed using the present methods.

Determination of Mercury:

A portion of solution (3 ml) containing an amount of mercury(II) in the range 0.25-20 ppm was transferred into a 5 ml volumetric flask. Then 0.6 ml of $K_4Fe(CN)_6$ was added followed by 0.1 ml ferrozine and the volume was completed with the buffer solution. The time for addition of $K_4Fe(CN)_6$ solution was taken as the zero time. The absorbance was measured at 562 nm after 5 min. against a reagent blank. A stopwatch was used to denote exact times.

Results and Discussion

Effect of pH:

The effect of pH on the absorbance of the experimental solution was studied in the pH range 2-8. The solutions were prepared as described in the general procedure. The results obtained showed that maximum absorbance can be obtained in the pH range 4.0-4.5 when the absorbance is measured after 5 min. A stopwatch was used to monitor the time.

Effect of $K_4Fe(CN)_6$ and ferrozine:

1.2×10^{3} and 2×10^{-4} M solutions of $K_4Fe(CN)_6$ and ferrozine were used in all runs since these are found to be the critical concentrations beyond which no further increase in absorbance was observed.

Temperature and Time:

In all runs a temperature of 30 C and a reaction time of 5 minutes were chosen. The temperature used was close to room temperature and a 5 min interval is practically short and adds to the importance of the method

Calibration graph:

Following the general procedure a linear relationship was obtained between the absorbance and the concentration of mercury(II) within the range 0.05-4.0 ppm with relative standard deviation of 3.4% for 10 g of mercury(II).

Effect of foreign ions:

The effect of foreign ions is presented in Table 1 and show that this method is quite satisfactory and suffer from lack of interferences. The tolerance limit was taken as the maximum amount of the foreign ion that cause an error of less than ±4% in the absorbance of the reaction mixture containing 2.5 ppm mercury(II).

Table 1

Effect of foreign ions.

Conditions: [$K_4Fe(CN)_6$] = $1.2x10^{3}$M, [Ferrozinc] = $2.0x10^{4}$M, [Mercury(II)] = 2.5ppm, pH=4.5, $_{max}$ = 562 nm, Temperature = 30°C, time= 5 min.

Foreign ion		Ion:Hg(II)	Absorbance	± % error*
ion	Conc. ppm	Mass ratio		
No ions present	--		0.48	--
Ni(II)	11.7	4.7:1	0.47	-2.1
	23.5	9.4:1	0.44	-8.3
	47.0	18.0:1	0.12	-75.0
Mg(11)	4.8	1.9:1	0.48	--
	9.7	3.9:1	0.44	-8.3
	19.4	7.8:1	0.39	-18.7
Zn(II)	13.0	5.2:1	0.47	-2.1
	26.0	10.4:1	0.43	-10.4
Cd(II)	22.5	18.0:1	0.46	-4.1
	45.0	36.0:1	0.43	-10.4
Pd(II)	4.2	1.7:1	0.49	+2.0
	8.4	3.4:1	0.51	+6.2
	17.0	6.7:1	0.51	+6.2
	34.0	13.4:1	0.52	+8.3
Co(II)	58.9	23.6:1	0.48	--
	117.8	47.1:1	0.46	-4.1
	235.7	49.0:1	0.44	-8.3
Cu(II), Pt(II),	101.7	40.6:1	0.46	-4.1
La(II), Ce(III),	up to 500	200.0:1	0.47	-2.0
Eu(III), Na(I)	up to 500			
K(I), Ca(II)	up to 500			
Al(III), Pb(II),	up to 500			
Th(IV), U(VI).	up to 500			
Cl^-, Br^-, ClO_4^-,	up to 500	200 :1	0.48	--
CH_3COO^-, SO_4^{2-},	up to 500	200:1		
NO_3^- ,Silicate,	up to 500			
Oxalate, Borate	up to 500			

* + Positive error, - negative error.

Applications:

The present method was applied to the determination of mercury in roots, stems, leaves and fruits of broad beans irrigated with water containing different amounts of mercury(II). The results obtained show that the uptake of mercury by the various parts of the plant increases by increasing the concentration of mercury(II) in the solution used for irrigation. On the other hand it was found that the uptake of mercury was higher in roots and leaves than in fruits and stems of the treated plants.

Evaluation of the method:

The results obtained using the present method showed that the detection limit of mercury is relatively very low (0.05 ppm). The detection limit which can be obtained using the conventional spectrophotometric methods is about 0.5 ppm(1). On the other hand the detection limit using a well established atomic absorption method is about 0.05 ppm although some techniques permit samples to be analyzed for mercury down to $2x10^{6}$ ppm using flameless cold vapor atomic absorption method(2). Also inductively coupled plasma mass spectrometry ICP-MS (3,4) is able to determine a wide range of elements including mercury with high sensitivity and a wide linear interval. However ICP-MS is only applicable to large central labs and the method presented in this work is simple and will work "in the field".

Therefore comparison among the above mentioned methods showed that the present method is relatively very sensitive and it permits food samples to be analyzed for mercury below the FDA tolerance limit which is about 0.5 ppm.

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