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SPECTROPHOTOMETRIC DETERMINATION OF ZN WITH 4-(2-PYRIDYLAZO) RESORCINOL

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4-(2-pyridylazo) resorcinol (PAR) reacts sharply with zinc to form a water soluble orange-red complex. This complex has constant absorbance at pH 9.2 - 10.6, and its maximum absorbance is at 493 mμ. It has very high sensitivity with a molar absorptivity of 8.3×10^4, and the complex obeys Beer's law up to 0.8 μg/ml. The composition of the complex is Zn: PAR = 1 : 2.

The effect of 38 coexisting ions was investigated, and it was found that indium, bismuth, copper, mercury(II), cadmium, yttrium, manganese, cobalt, and nickel interfere, however, indium and manganese can be masked by the addition of sodium pyrophosphate while bismuth and yttrium can be masked with sodium tartarate and sodium fluoride respectively. It is possible to combine the procedure with an ion exchange separation to determine trace levels of zinc in the presence of large quantities of copper, manganese, cobalt, and nickel.

1. Introduction

The authors reported on the determination of cadmium with 4-(2-pyridylazo) resorcinol[1], and this paper describes an attempt to use the same reagent for the determination of Zinc.

When Pollard et al.[2] were working on the spectrophotometric determination of cobalt, lead, and uranium with PAR, they observed that zinc formed a light red complex with this reagent. Iwamote[3] looked into the composition of this complex and reported it to be Zn : PAR = 1 : 1, however, he did not

follow up this work with a determination of zinc. The authors tested the spectrophotometric determination of zinc with this reagent and found that this is a very sensitive reaction that is associated with a molar absorptivity of 8.3×10^4, and its sensitivity per 0.001 absorbance is 0.0008 $\mu g/cm^2$. This sensitivity is twice that of dithizone[4] (0.0016 $\mu g/cm^2$) three times that of zincon[5] (0.003 $\mu g/cm^2$), and twice that of xylenol orange[6], (0.0018 $\mu g/cm^2$). It has decidely superior sensitivity compared to other reagents like α, β, γ, δ-tetraphenyl porphin[7], 2-(2-hydroxy-5-methoxphenylazo)-4-methylthiazol[8], 9-quinolinol[9], and chromazurol S[10]. The color is stable, and this reagent was found to be quite suited to the determination of zinc. The composition of the complex was found to be zinc : PAR = 1 : 2 which is quite different from the value reported in the literature[3].

PAR has been used as a color forming reagent with cobalt[2,11,12], lead[2,15] indium[16,17]. niobium[18,19], iron[20], nickel[21], manganese[22,23], and copper[24]. Thus, the property of PAR to form complexes with many metal ions poses the problem of selectivity, and the presence of diverse ions becomes a major problem that has to be resolved in any quantitative method of zinc with this reagent. The authors studied the effect of various masking agents and buffer systems as a result of which it was discovered that the reaction of zinc and PAR in the presence of a citrate salt and in a carbonate buffer would involve no sacrifice in sensitivity and color stability yet enable an absorption maxium extending over a fairly wide range of pH and allow the determination to be made in the presence of coexisting ions like gallium, tin(IV), lead, and iron(II,III). It was also found that the addition of sodium pyrophosphate will mask out indium and manganese while sodium tartarate will mask bismuth

and sodium fluoride yttrium. It is possible to determine trace levels of zinc in the presence of large amounts of copper, manganese, cobalt, and nickel by introducing an ion exchange separation. As a result, only two ions, cadmium and mercury(II), were found to be the only interferences of 38 diverse ions that were tested.

We feel from the results described above that this method can be applied effectively to the spectrophotometric determination of trace levels of zinc.

2. Reagents and Apparatus

2.1 Reagents

Standard zinc solution. Reagent grade zinc nitrate was dissolved in water to prepare a solution containing about 1 mg/ml zinc. This solution was standardized by a chelatometric titration with XO indicator. This standard solution was diluted to appropriate levels for the work that follows.

PAR solution. Dotite PAR obtained from the Dojin Chemical Company was used. Fifty milligrams of this reagent was dissolved in 4 ml of 0.5% sodium hydroxide solution and then diluted to 100 ml with water.

Buffer solution: A 0.2 mol/liter sodium bicarbonate solution and a 0.2 mol/liter sodium carbonate solution were mixed and adjusted to the desired pH.

Sodium citrate solution: Reagent grade sodium citrate was dissolved in water and made up to a strength of 1 mol/liter.

Other reagents: All reagents were reagent grade material.

2.2 Apparatus

Determination of absorbance: A Hitachi-Perkin Elmer Model 139 spectrophotometer was used (optical path length 10 mm in a glass cell).

Determination of pH: A Hitachi-Horiba Model M-5 pH meter was used.

3. Procedure

A sample solution containing up to 40 µg zinc was placed in a 50-ml volumetric flask after which 10 ml of 1 M citric acid solution was added followed by 3 ml of carbonate buffer solution to adjust the pH to 9.7. Next 2 ml of 0.05% PAR solution was added to develop the color. The volume was then made up to 50 ml. A blank was run at the same time using all the reagents but excluding the zinc. The absorbances were determined at 493 mµ.

4. Experimental Results

4.1 Absorption curve of the complex

The procedure described in section 3 was used to develop color with 20 µg of zinc, and the reagent blank was used as the reference solution for the determination of the absorbance at 447-565 mµ. At the same time, the absorption of the blank was determined with water as the reference. The absorption curves obtained at different pH are shown in Fig. 1.

The maximum absorbance of the zinc complex occurred close to 493 mµ, and this peak was little affected by pH between 8.0 and 10.3. Consequently it is believed that the composition of the complex is unaffected in this pH range. At the same time, the absorption of the PAR itself is relatively small in this region, so the wavelength of 493 mµ was selected for this determination.

4.2 Effect of pH

The relationship between the absorbance of the complex at 493 mµ and the pH was determined following the procedure described in section 3, and the pH range of 6.2 - 12.2 was studied. The carbonate buffer was used in the pH range 9.0 - 11.2 while pH levels below 9.0 were adjusted with 0.1 N HCl and pH levels above 11.2 with 0.1 N NaOH. The results are shown in Fig. 2.

The absorbance of the complex exhibits a sharp increase near pH 7.3 - 9.0 and attains constancy and its maximum value at pH 9.2 - 10.6 and then begins to lose its intensity above pH 10.6. In another direction, the absorbance of PAR is nearly constant between pH 8.5 - 10.0 and increases sharply from pH 10.0 and above. As a result, pH 9.7 was selected as the working level for this method. The absorbance of the complex was constant and maximum between pH 9.2 - 10.2 when sodium citrate was not added, but the pH range of maximum and constant absorption was extended to the alkaline as high as 10.6 when sodium citrate was added. No such effect was observed with the addition of sodium tartarate or sodium fluoride.

4.3 Stability of the color

The complex was formed using 20 µg of zinc according to the procedure described in section 3, and the changes in time of its absorbance was followed. The results are shown in Fig. 3.

Zinc forms a complex with PAR very rapidly, and the absorbance of the complex becomes maximum after a fixed period to remain unchanged for at least 3 hours. Similar results were obtained when the carbonate buffer was replaced with ammonia or borate buffer and when sodium tartarate or sodium acetate was used in place of sodium citrate.

4.4 Effect of amount of reagent added

Only the addition of PAR was varied as the procedure of section 3 was followed, and the absorbances of the complexes so formed were measured. The results are shown in Fig. 4.

The addition up to 0.5 ml of 0.05% PAR to 20 µg of zinc resulted in sharp increases in the absorption, and the maximum absorbance was obtained with the addition of 0.7 ml. Further addition of PAR reagent caused no change in the absorbance at least up to 6 ml. These results tell us that the addition of greater than 0.7 ml of 0.05% PAR reagent will produce the desired complex in a quantitative manner. An addition of 2 ml was decided as the reagent volume.

4.5 Effect of amount of buffer added

The absorbance of the complex remained constant with buffer solution prepared from 0.2 mol/liter sodium bicarbonate and 0.2 mol/liter sodium carbonate while the addition was varied between one and 20 ml. It was decided to add 3 ml of the buffer to adjust the pH to 9.7.

4.6 Effect of the volume of sodium citrate solution added

The effect of the addition of 1 mol/liter sodium citrate solution between 0-20 ml was followed as far as the absorbance was concerned. The results indicated that the absorbance remained essentially constant in this range of addition, but the absorbance of the reagent blank began to increase slightly with an addition of 13 ml or more. The addition of an excessive amount of sodium citrate was associated with a trend toward some changes in the absorbance with time. This addition increased the viscosity of the solution to the extent that any bubbles formed were difficult to dissipate and presented an interference to the measurement. Taking into account the effect of coexisting ions, the addition of sodium citrate solution was speciifed to be 10 ml.

4.7 Working Curve

The results described in the above paragraphs were utilized to construct a working curve following the procedure of section 3. This curve is shown in Fig. 5.

The curve is seen to be linear up to zinc content of 0.8 µg/ml, and Beer's law is closely obeyed. The reproducibility also is good. The molar absorptivity was found to be 8.3×10^4, and the sensitivity per 0.001 absorbance is 0.0008 which is very sensitive.

4.8 Composition of the complex

Iwamoto[3] reported this complex to have a composition of Zn : PAR = 1 : 1 at pH 10.0. The authors studied the composition of this complex at pH 9.7 using the mol ratio and continuous variation methods and found the composition to be Zn: PAR = 1 : 2. The results of measurements made at 493 and 530 mµ are shown in Fig. 6 and Fig. 7. The PAR concentration was fixed at $1.836 \times 10^{*-5}$ mol/liter while the mol ratio of zinc was varied in the mol ratio method. The aggregrate concentration of the zinc and PAR was built up to 3.672×10^{-5} mol/liter in the continuous variation method.

4.9 Effect of coexisting ions

The effect of different coexisting ions on the determination of 20 µg of zinc was determined. The addition of diverse ion was limited to 1 mg, and the procedure of section 3 was followed to measure the absorption. The results are listed in Table 1. Among the 38 ions that were tested, the alkali metals, alkaline earth metals, aluminum, thallium(I), zirconium, hafnium, and vanadium comprised part of the 19 ions whose addition at the 1 mg level results in relative error less than 5%. This represented a 50 fold excess of diverse ion. Thorium can be present in 25 fold excess; gallium, tin(IV), iron(II,III) palladium, platinum, and cerium(III) in 5 fold excess; and lead

and chromium(III) in equivalent quantity with no adverse effects. This procedure calls for the use of a citrate salt as an auxiliary chelating agent and a carbonate buffer which seems to be effective in masking the effects of gallium, tin(IV), lead, and iron(II,III). It was found when a phosphate salt, tartarate, or acetate was used in place of the citrate and borate or ammonium buffer in place of the carbonate buffer that the above mentioned elements interfered badly. The elements that are left that interfere with this method are indium, bismuth, copper, mercury(II), cadmium, yttrium, manganese, cobalt, and nickel. The addition of 5 ml of 5% sodium pyrophosphate will mask 5 fold excess of indium and manganese. The addition of 10 ml of 1 mol/liter sodium tartarate will mask a 5 fold excess of bismuth while 5 ml of 2% sodium fluoride will mask the equivalent quantity of yttrium.

4.10 Separation and determination of zinc in the presence of copper, manganese, cobalt, and nickel

The use of an ion exchange separation method to separate and determine trace levels of zinc in the presence of large amounts of coexisting copper, manganese, cobalt, and nickel was tested. Among these 5 ions zinc is the only ion that forms chloro complexes in low concentration hydrochloric acid solution which suggests a possible means of separation.[25,2,6] Either a cation or anion exchange separation can be adopted, but the anion exchange method requires less resin because it involves the passing through of the large excess of coexisting ions while retaining the desired zinc complex. This will require only a comparatively small volume of solution to wash the resin and solubilize the zinc and also reduce the time required. The anion exchange method was tested for the separation of zinc from 2500 fold excess of manganese,

copper, cobalt, and nickel followed by the spectrophotometric determination of the zinc. The satisfactory results shown in Table 2 were obtained. This method is readily reproducible and very convenient.

Procedure: Test solution prepared in 0.5 N hydrochloric acid was passed through a Dia-ion SA No. 100 (strongly basic anionic ion exchange resin, chloride form) column (11 mm diameter, 45 mm height, packed with resin) at a flow rate of 2 ml/min to sorb the zinc complex. The column was washed with 0.5 N hydrochloric acid to insure the complete removal of the other metal ions after which the zinc was removed with distilled water. The eluent was then used in the spectrophotometric procedure described in section 3.

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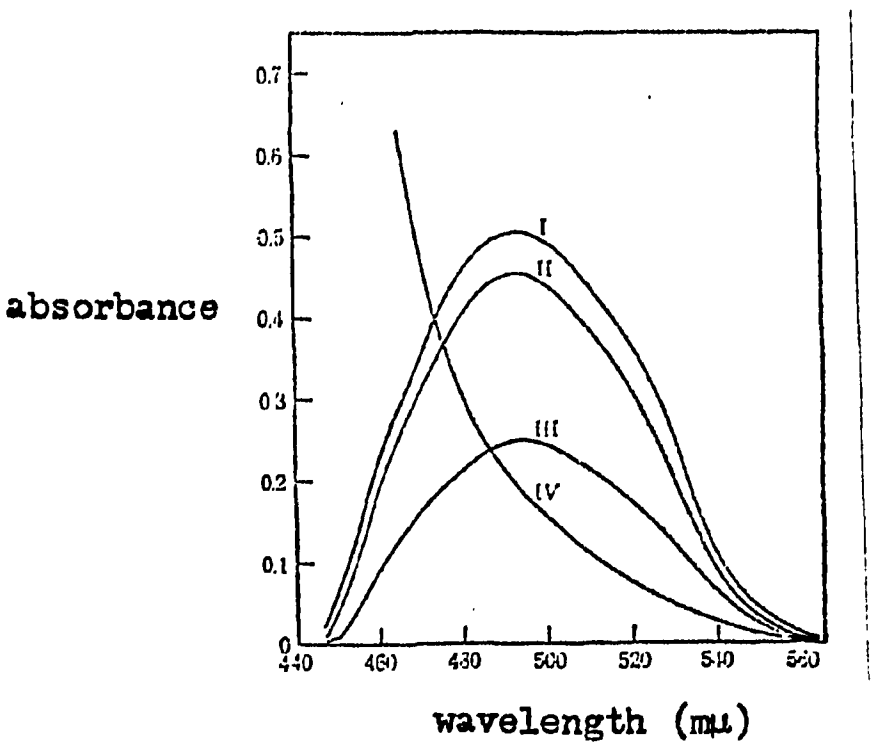
Table 1 Effect of Coexisting Ions

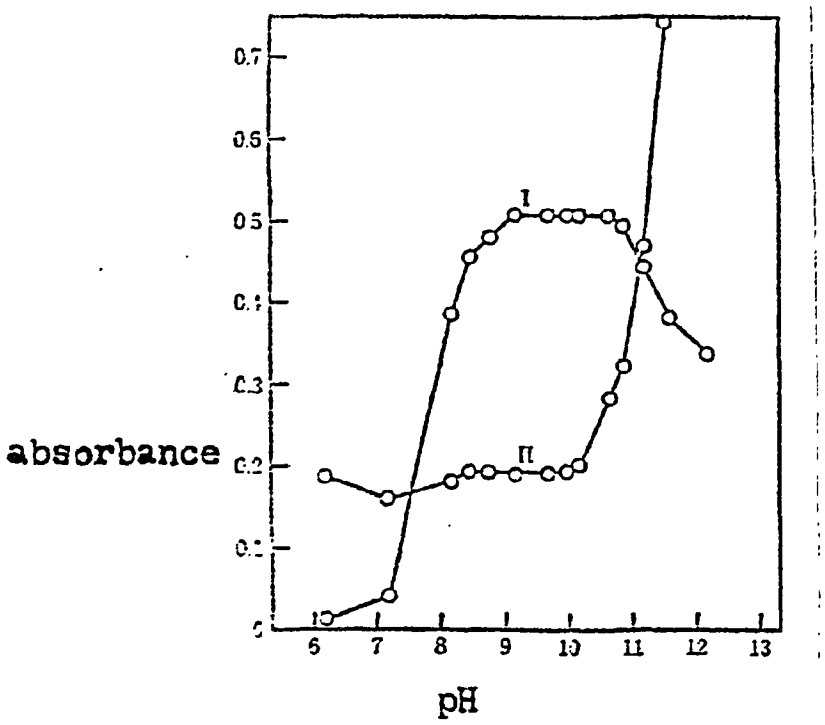
Added Ion	Amount Added (mg)	Zn Found (μg)
—	—	20.0
Li^{+}	1	21.0
K^{+}	1	20.0
Be^{2+}	1	19.0
Mg^{2+}	1	20.0
Ca^{2+}	1	19.9
Sr^{2+}	1	19.6
Ba^{2+}	1	20.0
Al^{3+}	1	19.7
Ga^{3+}	0.1	20.3
In^{3+}	0.02	24.0
a)	0.1	20.9
Tl^{4+}	1	20.8
Sn^{2+}	0.1	19.5
Pb^{2+}	0.02	20.2
As(V)	1	20.0
Sb^{3+}	1	19.4
Bi^{3+}	0.02	21.6
b)	0.1	20.5
Cu^{2+}	0.02	35.4
Au^{3+}	1	21.0
Hg^{2+}	0.02	23.9
Cd^{2+}	0.02	28.9
Y^{3+}	0.02	21.4
c)	0.02	20.4
Zr^{4+}	1	20.5
Hf^{4+}	1	20.8
V(V)	1	20.1
Cr^{3+}	0.02	19.4
Mo(VI)	1	19.3
W(VI)	1	19.8
Mn^{2+}	0.02	25.4
a)	0.1	20.7
Fe^{2+}	0.1	20.8
Fe^{3+}	0.1	19.7
Co^{2+}	0.02	32.8
Ni^{2+}	0.02	31.8
Rh^{3+}	1	20.0
Pd^{2+}	0.1	20.4
Os^{3+}	1	20.5
Pt(IV)	0.1	19.8
Ce^{3+}	0.1	20.4
Th^{4+}	0.5	21.0

Notes: a) 5 ml of 5% sodium pyrophosphate added
b) 10 ml of 1 mol/l sodium tartarate added
c) 5 ml of 2% sodium fluoride added



I: Zn-PAR complex (Vs. blank), pH 9.7
II: Zn-PAR complex (Vs. blank), pH 8.5
III: Zn-PAR complex (Vs. blank), pH 7.9
IV: Reagent blank (Vs. water), pH 9.7

Fig. 1 Absorption curves of Zn-PAR compl x and PAR



I: Zn:PAR complex (Vs. blank)
II: Reagent blank (Vs. water)

Fig. 2 Effect of pH

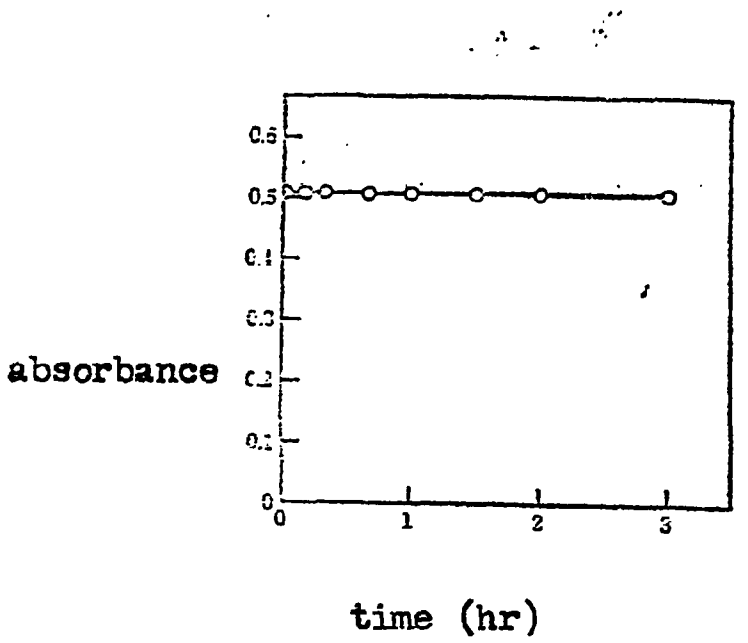


Fig. 3 Stability of color

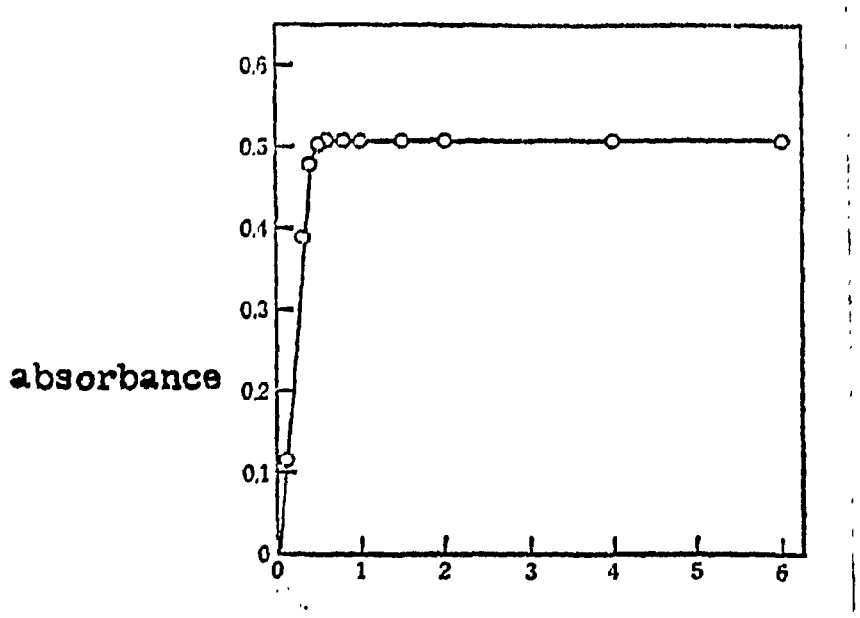


Fig. 4 Effect of amount of reagent added

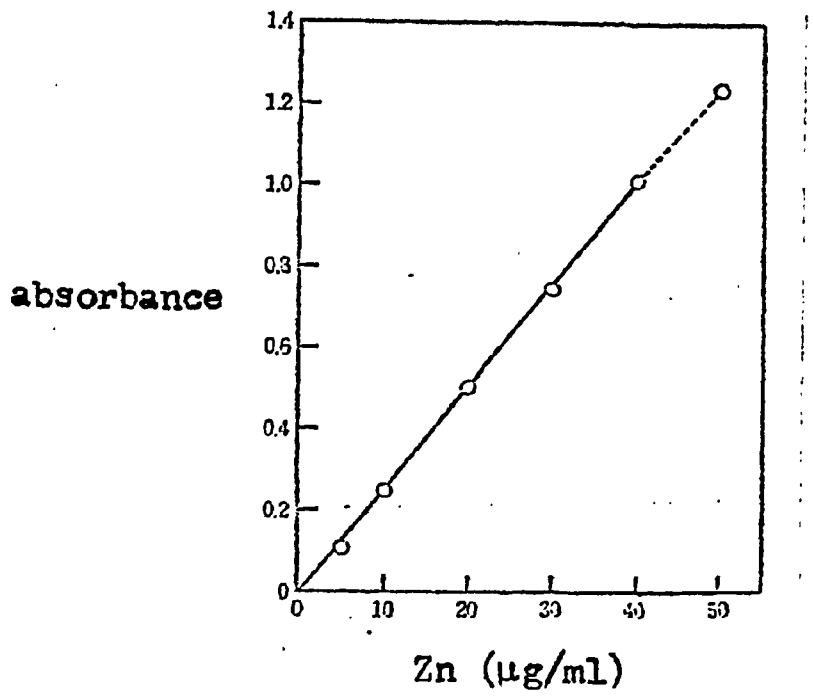
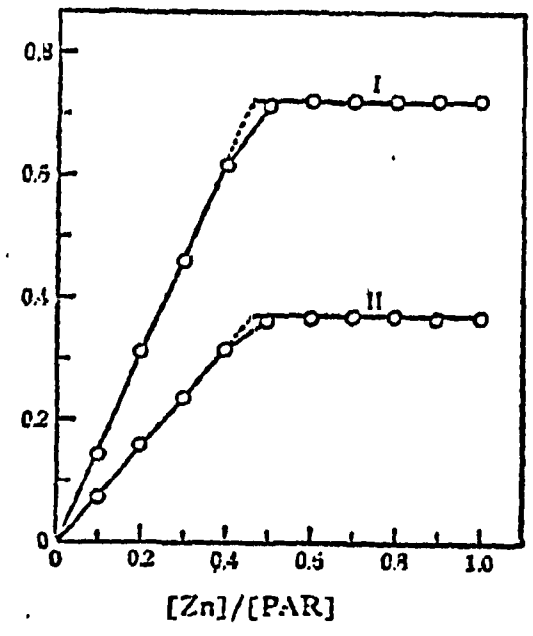


Fig. 5 Working curve

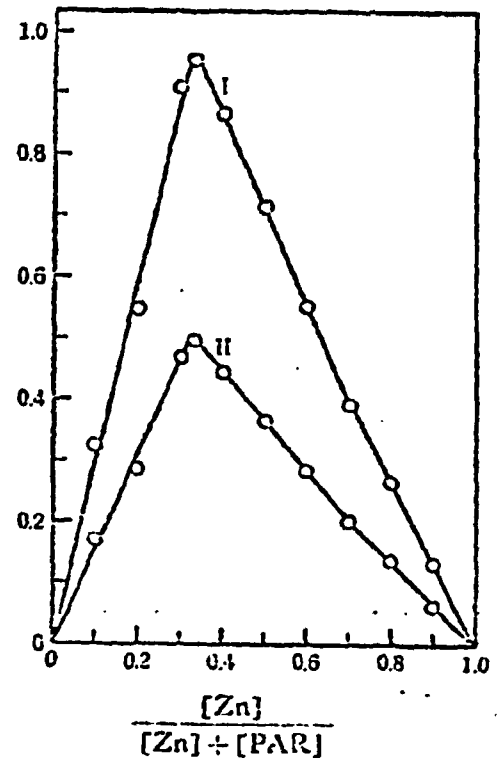
absorbance



PAR = 1.836×10^{-5} mol/l
I: measured at 493 mμ
II: measured at 530 mμ

Fig. 6 Composition of complex by the mol ratio method

absorbance



Zn + PAR = 3.672×10^{-5} mol/l
I: measured at 493 mμ
II: measured at 530 mu

Fig. 7 Composition of complex by the continuous variation method

Table 2 - Removal of Coexisting Ions by Anion Exchange Resin

Ion Present	Amount (mg)	Salt Added	Zn Found (μg)
—	—	—	20.0
Cu^{2+}	50	$CuCl_2$	19.8
Mn^{2+}	50	$MnCl_2$	20.0
Co^{2+}	50	$CoCl_2$	20.6
Ni^{2+}	50	$NiCl_2$	19.6
Cu^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}	[1]50	[2]	21.0

Key: 1. each
2. same as above