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Selective Spectrophotometric Determination of Zinc with Di-2-pyridylmethanone 2-Pyrimidylhydrazone

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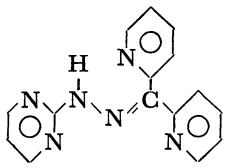
Synopsis. Synthesis of a new 2-pyrimidylhydrazone *i.e.* di-2-pyridylmethanone 2-pyrimidylhydrazone (DPMPH) and its application in the selective determination of micro-amounts of zinc is presented. DPMPH reacts with zinc to form a yellow complex in the pH range 7.9—11.1 with molar absorptivity 5.2×10^4 l mol^{-1} cm^{-1} at 430 nm. Beer's law is obeyed upto 1.56 ppm of zinc. Zinc has also been determined in several alloys.

In recent years many nitrogen containing heterocyclic hydrazones derived from 2-hydrazinopyridine[1-4] and 2-hydrazinoquinoline[5-8] have been prepared and tested as possible analytical reagents. Lions *et al.*[9,10] first reported the analytical properties of these compounds. However, hydrazones derived from 2-hydrazinopyrimidine have not been investigated in detail for analytical purpose.

In this note, synthesis of di-2-pyridylmethanone 2-pyrimidylhydrazone (DPMPH, I) and its application in the determination of micro-amounts of zinc is described.



DPMPH, I

This method is based upon a differential demasking technique proposed by Platte and Marcy.[11] According to this technique utilized here zinc was determined with DPMPH in the presence of interfering metals, such as iron and copper. The cyanide complexes of the metals present in the solution were formed and the zinc complex was preferentially destroyed by chloral hydrate. The zinc–DPMPH complex formed by the liberated zinc was measured spectrophotometrically, before interfering metals were liberated from its cyanide complex. It was reported[12-14] that the cyanide complexes of Cu(II) and Fe(III) are not stable enough to prevent interferences of copper and iron in the determination of zinc according to the above procedure and the reduction of Cu(II) and Fe(III) with ascorbic acid was proposed.[15] The Cu(I) and Fe(II) cyanide complexes are more stable against chloral hydrate.

Experimental

Apparatus. A Unicam SP600 spectrophotometer was used for measuring absorbance and a Beckman Expandomatic SS-2 pH meter was used for pH measurements.

Reagents. *Synthesis of Di-2-pyridylmethanone 2-Pyrimidylhydrazone*: 2-Chloropyrimidine was prepared by the method of Kogon *et al.*[16] and converted to 2-hydrazinopyrimidine by the method of Shirakawa *et al.*[17] An ethanolic solution of equimolar quantities of 2-hydrazinopyrimidine and di-2-pyridylmethanone (Fluka A. G.) was refluxed for 6 h. The residue obtained after the removal of ethanol, by using a rotatory evaporator, was crystallized from benzene to give pale yellow crystals (mp 160 °C). Purity was checked by TLC. Elemental analysis confirmed the synthesis (Calcd: C, 65.2; H, 4.3%. Found: C, 65.5; H, 4.9%).

DPMPH solutions were prepared in ethanol (95%) and stored in amber glass bottles. Such solutions are stable for several weeks.

Ascorbic Acid Solution (10% w/v): This solution was prepared on alternate days and stored in amber glass bottles.

Buffer Solution: Borax (4.5 g) and KCN (0.2 g) were dissolved in 20 ml of 4 M NaOH and the solution was diluted to 50 ml with distilled water. When 1 ml of buffer is mixed with 5 ml of working standard or blank, the resulting pH should fall between 8.5—9.5 usually. If it does not, the preparation must then be repeated by changing the amount of alkali added and the pH is checked again. Once the final conditions have been established for this solution, it is easy to prepare new buffer when it is needed.

Standard Zinc Solution: A standard solution of zinc was prepared by dissolving the analytical reagent grade zinc sulfate heptahydrate in doubly distilled water.

Chloral Hydrate Solution (1.5%): Chloral hydrate solution was prepared for differential demasking of zinc from cyanide complex.

All other solutions were prepared with analytical grade reagents in doubly distilled water.

Recommended Procedure. To an aliquot containing 2.6—13.0 μg of Zn(II), add 1 ml of ascorbic acid solution, followed by 2 ml of buffer solution. Then add 1 ml of ethanolic 10^{-2} M solution of DPMPH and dilute the contents to 10 ml. Measure the absorbance of the solution within 25 min after the addition of DPMPH at 430 nm against reagent blank prepared under the identical conditions.

Absorption Spectra, Effect of pH *and Reagent Concentration*: A pH study of the complexation of DPMPH with Zn(II) showed that the yellow complex (λ_{max}=430 nm) gives a constant absorbance in the pH range 7.9—11.1. Carrying out the proposed procedure it has been found that the pH adjustment in the desirable range was more effectively achieved when the buffer solution and the masking agent *i.e.* the cyanide, are added simultaneously. It was observed that a separate addition of cyanide and buffer, irrespective of their order of addition, did not give good results in pH adjustments. For complete complexation 6-fold excess of reagent is necessary. The absorbance of the reagent at the wavelength of maximum absorbance of its zinc complex *i.e.* at 430 nm, is negligible. This is advantageous because the excess of reagent is not critical.

Stability of the Complex. It was also observed that addition of chloral hydrate is not necessary after the addition of DPMPH, for the destruction of zinc–CN complex and for full colour development. The zinc–CN complex is completely

destroyed within 5 min and zinc–DPMPH is formed even in the absence of chloral hydrate. This must be related to the strength of the stability constants of zinc–CN and zinc–DPMPH complexes. This complex is stable upto 25 min. While by addition of chloral hydrate (1.5%) solution, zinc–DPMPH complex is formed as soon as it is added and remains stable for 5 min, then it diminishes. However, full colour development takes place in both the cases. Hence readings of the absorbance of the test solution should be taken within 5—25 min after the addition of DPMPH in the first case and within 5 min in the second case.

Effect of Diverse Ions: Synthetic solutions containing known amounts of zinc(II) and varying amounts of diverse ions were prepared and the recommended procedure was followed for the determination of zinc(II). An error of $\pm 2\%$ in the absorbance reading was considered tolerable. In the determination of 0.65 ppm of zinc, the ions tolerated (given in ppm in parentheses) are as follows:

Chloride, bromide, iodide, fluoride, citrate, tartrate, thiourea, acetate, sulfite, nitrite, nitrate (2000 ppm each); thiocyanate (1000 ppm); thiosulfate, oxalate (500 ppm each); phosphate (150 ppm); Ca(II), Sr(II), Ba(II), Mg(II), Pb(II), Mo(VI), W(VI) (1000 ppm each); Al(III), Sn(II), Be(II), Sb(III), (800 ppm each); Ru(III), Rh(III), Ir(III), Au(III), Os(VIII), Ti(IV), Mn(II), Ag(I) (500 ppm each); Pd(II), Ni(II), Co(II), Cd(II), Hg(II), V(V) (200 ppm each); Cu(II) and Fe(II) (100 ppm each). However, EDTA interferes seriously.

Calibration Curve: Beer's law is obeyed upto 1.56 ppm of Zn(II) in presence or absence of chloral hydrate. The optimum concentration range evaluated by Ringbom's method is 0.26—1.30 ppm. The Sandell's sensitivity is 0.0012 μg Zn cm^{-2} and the molar absorptivity is 5.2×10^4 l mol^{-1} cm^{-1} at 430 nm. The composition of the complex as determined by Job's method of continuous variations shows that metal to ligand ratio is 1 : 2.

Determination of Zinc in Alloys. Dissolve 1.0 g of brass or gun metal in 10 ml of concentrated nitric acid, evaporate to dryness, extract with 4 ml of concentrated sulfuric acid and dilute to 250 ml.

Table 1. Determination of zinc (in %) in alloys

Alloy	Zn reported	Zn found	n[a)]	R.s.d. (%)
Brass (BCS No. 5g)	30.0	29.8	6	1.40
Gun metal (BCS No. 6g)	1.5	1.43	6	2.96
6% Zn–Al alloy (BCS No. 300)	5.98	5.76	6	1.49

a) The average of n determinations is reported with the relative standard deviation.

Dissolve 1.0 g of the aluminium alloy in aqua regia, evaporate to small volume, add 10 ml of concentrated hydrochloric acid and dilute to 250 ml.

Suitable aliquot solution is taken and recommended general procedure is followed for the determination of zinc in alloys. The results of alloy analysis are summarized in Table 1.

Selective and sensitive method for the determination of zinc is proposed. Determination can be carried out in aqueous solutions and there is no need of extraction *etc.* Zinc can be determined in alloys, without its separation from other metals present in the alloys.

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