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SPECTROPHOTOMETRIC DETERMINATION OF IRON(III) BY SYNERGISTIC EXTRACTION WITH N-HYDROXY-N-*m*-TOLYL-N′-α-NAPHTHYL-BENZAMIDINE HYDROCHLORIDE AND THIOCYANATE

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Thiocyanate method[1] is frequently used for the determination of iron which is simple, rapid and sensitive but suffers from various experimental limitations such as amount of thiocyanate, non-linearity of Beer's law, time of standing, reproducibliity, etc. Phenanthroline method[2] and tripyridyl method[3] recommended for spectrophotometric determination of iron(III) are subject to serious interference of many common ions. N-Hydroxy-N,N′-diarylbenzamidines are new type of organo-analytical reagents useful for gravimetric and spectrophotometric determination of transition metals[4–6]. In the present investigation a newly synthesised reagent, N-hydroxy-N-*m*-tolyl-N′-*α*-naphthylbenzamidine hydrochloride (HTNBH) is employed for the extractive photometric determination of iron (III). The method based on this colour reaction is free from strict control of experimental variables. This highly selective method affords the separation of iron(III) as orange-red complex from nickel, cobalt, chromium, lead, cadmium, zinc, etc., in a single extraction with benzene which makes the method suitable for determination of microgram quantities of iron.

A (Carl Zeiss 'Specord' ultraviolet-visible spectrophotometer with matched 1 cm quartz and silica cuvettes) was employed for recording the spectra.

HTNBH was prepared by the condensation of equimolar quantities of N-*α*-naphthylbenzimidoyl chloride and N-*m*-tolyl-hydroxylamine in ether[7]. The resulting hydrochloride was crystallised from absolute alcohol. M.P. 166°C; yield, 80%. Elemental analysis (found C, 74·07; H, 5·59; N, 7·09; calculated for $C_{24}H_{21}N_2OCl$: C, 74·13; H, 5·40; N, 7·21%). A 0·1% w/v solution of HTNBH in benzene was used for extraction purposes.

An aliquot of iron(III) solution containing 100 μg of metal was placed in a separatory funnel. To this 2 ml of 5% potassium thiocyanate solution was added. The acidity of the solution was adjusted to 0·2–0·6 M with 2 M HCl and diluted to 25 ml. Then added 25 ml of 0·1% solution of HTNBH in benzene and equilibriated for 2 min. Dried the benzene extract over anhydrous sodium sulphate and measured the absorbance at λ_{max} of the complex.

The reagent shows negligible absorbance in the region 450–700 nm. The Fe(III)–HTNBH–$SC\bar{N}$ ternary complex shows λ_{max} at 460–470 nm with molar absorptivity 11620 ± 50 l. mole^{-1} cm^{-1}. The various solvents like benzene, chloroform, toluene, carbon tetrachloride, etc., were tried, benzene was found to be the best solvent as the complex showed high distribution ratio in it. The optimum acidity range was found to be 0·2–0·6 M HCl. The colour development was instantaneous and the extraction was complete within 2 min. The extracted chelate was stable for nearly 2 days at 20–40° C. The order of addition of reagent was not critical. A 25 fold molar excess of HTNBH and 130 fold molar excess of thiocyanate were necessary for complete extraction of the complex. Excess of HTNBH and thiocyanate did not interfere in the determination. The system obeys Beer's law over the concentration range 0·6–4·8 ppm of iron(III). The effective concentration range evaluated from Ringbom curve was 1·0–4·0 ppm. The Sandell's sensitivity of the colour reaction was 0·0048 μg Fe cm^{-2}. The Precision of the method was checked by measuring the absorbance values of 10 samples each containing a final concentration of 2 ppm of iron(III). The mean absorbance was 0·415 with standard deviation ±0·0023.

In Fe(III)–HTNBH–$SC\bar{N}$ mixed chelate the ratio of iron(III) to HTNBH and $SC\bar{N}$ were determined by curve fitting method[8]. (log absorbance *vs.* log M of HTNBH[8]$SC\bar{N}$). The results obtained showed the formation of 1:1:2 (metal : reagent : thiocyanate) ternary complex in benzene.

To study the influence of foreign ions, varying amounts of diverse ions were mixed with 2 ppm of iron at 0·3 M HCl concentration and the extraction ewas carried as described above. Chloride, bromide, ammonia, thiourea, phthalate, nitrate, sulphate, alkali and alkaline earth metals and lanthenoid elements did not interfere upto 3000 ppm. The tolerance limit of

other ions causing an error less than 2% are given in parenthesis (in ppm): Fe^{2+}, Co^{2+}, Co^{2+}(800); Cr^{3+} (600); Ni^{2+}, Zn^{2+}, Cd^{2+} (1,500); V^{5+}, Ti^{4+}(50); Pb^{2+} (600); Mn^{3+} (600)[a]; Zr^{4+}(400); W^{6+}(200); PO_4^{-3} (1,200); F (1,500); AsO_3^{3-} (1,200); UO_2^{2+} (600); Mo^{6+}(15); Ta^{5+} (200); $S_2O_3^{2-}$ (100); $C_2O_4^{2-}$ (800); I (600) Triethanolamine (400).

[a] In presence of sodium persulphate.

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EARLY DIAGNOSIS OF KRESEK (WILT) PHASE OF BACTERIAL BLIGHT OF RICE

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The Kresek (wilt) phase of bacterial blight is a serious stage of the disease of rice crop in tropical countries. The Kresek symptom develops due to systemic infection of the host by *Xanthomonas oryzae* (Uyeda and Ishiyama) Dowson, the incitant of the disease[5]. The infected young plants die suddenly after transplanting especially under highly favourable conditions in the monsoon season. The wilting of the affected plants eventually leads to severe economic losses in certain localities. The leaves of Kresek affected plants become greyish-green, wither and the seedling dies due to internal spread of the pathogen. The control of Kresek phase insures elimination of incidence of the leaf blight phase to a greater extent[5].

For effective control of the disease, it is necessary to know the early stage of symptomatological features in Kresek development. In order to derive this information the Kresek (wilt) phase was developed artificially by an improved root exposure inoculation technique, identified by the author. Twenty-five day old seedlings of a susceptible variety (IR 8) were used in the experiment. The root system of the seedlings was wounded by cutting the tips of roots, surface sterilized in 70% alcohol and exposed to heavy inoculum pressure (10^8 bacterial cells per ml). The inoculated seedlings were transplanted in plastic pots (16 × 15 cm size) filled with silty clay loam soil at the rate of 5 seedlings per pot. The experimental plants were grown in greenhouse as per standard practice. The plants showing positive response to the treatment were marked and the sequential development of symptoms of the Kresek (wilt) phase was carefully examined. In parallel with progressive development of the disease, the presence of the pathogen in the system of the plant was examined microscopically by bacterial exudation technique[3]. The diagnostic features of the disease are as follows:

The earliest symptom of the Kresek phase was observed as 'mid-vein yellowing' in the lower leaves as long continuous yellowish-green stripe after three weeks of transplanting of the inoculated seedlings. The yellow stripe occasionally appeared in between mid-vein and one of the margins of the leaf blade. The leaves with yellow stripes characteristically drooped from the diseased stool of the plant (Fig. 1). The bundles of the yellow stripe portion of the leaf carried heavy bacterial mass as revealed by intense streaming[5]. The yellow stripe assumed light brown in the leaves and margins of such leaves curled along the midrib. As the disease advanced the leaves rolled and turned to greyish-green. In the meantime the symptom appeared in the developing leaves also, the youngest being the most sensitive. The bacterium was present in such portions of the plant also. The later stage of Kresek development include browning of leaves of infected tillers, partial or total wilting of infected stools and emergence of smaller panicles from few residual tillers of partially wilting stools. The youngest leaf in the infected tiller is highly sensitive to systemic invasion of the pathogen.

Reitsma and Schure[4] observed yellowing of leaves in Indonesia. The presence of the bacterium in the infected plant was indicated[4]. Yoshimura and Iwata[6] considered dehydration, etiolation and floating of