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A HIGHLY SELECTIVE AND RAPID SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF IRON(II) WITH 4-(2-THIAZOLYLAZO)RESORCINOL

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4-(2-Thiazolylazo)resorcinol reacts sensitively with iron(II) to form a water-soluble brown complex, which spectrally has the selective absorption at 730 nm. The absorbance is constant at pH 8.9 to 10.3 and Beer's law holds up to 120 μg of iron(II). Many ions can be tolerable, especially 3d type metals. This method is comparable to that of 1,10-phenanthroline.

4-(2-Thiazolylazo)resorcinol(TAR) is known as a sensitive reagent for the spectrophotometric determination of metal ions.[1-3] In a previous work, we examined the extraction behaviors of 3d type metal(II)-TAR chelates with zephiramin[4] and recognized that TAR was superior as an ion-pair extraction reagent, especially for cobalt(II).[5] Meanwhile, we also found the peculiar property of the iron(II)-TAR complex, that was, it had the absorption at appreciably longer wavelength and was not extractable into organic solvents. Based on this observation, we investigated the fundamental conditions for the determination of iron(II) and established a simple and selective spectrophotometric method.

A recommended procedure is as follows: Transfer 3 ml of 0.1 % ascorbic acid and 5 ml of 0.05 % TAR aqueous-ethanol(1:1) solution into a 50-ml volumetric flask. Add a sample solution containing iron up to 120 μg and adjust the pH to 9.2 with 5 ml of 1 M ammonia buffer solution. After making up to volume with water, measure the absorbance at 730 nm against water. Care must be taken in adding order of TAR and sample solutions, otherwise the absorbance would decrease about 20 %.

The absorption spectra of iron(II) and nickel(II) complexes of TAR and a reagent blank are shown in Fig. 1. Iron complex has two absorption maxima at 547 nm and 730 nm, while the other 3d type metal(II) complexes have only one maximum near 540 nm and nickel shows it at 543 nm. We could not observe the metal-TAR complex which showed the absorption over 700 nm, hence this maximum at 730 nm is thought to be the specific absorption for iron(II). Besides, iron(III) complex does not absorb. By utilizing this, the state analysis of the dissolved iron(II) and iron(III) may be possible. As TAR blank shows no absorption above 640 nm, one might expect the enhancement of the accuracy on the determination of iron(II). The combining ratio of iron(II) to TAR in the complex was found to be 1:2. Since the complex is water-soluble, it must be a charged complex, but was not extracted into organic solvents even if variety of cationic, anionic and non-ionic surfactances were added. This facts suggests that the hydroxyl group or other ligands would participate in the complex, or iron complex itself would take the peculiar configuration. A constant absorbance is obtained in the pH range from 8.9 to 10.3, and below pH 7, iron(II) forms neutral complex with TAR. A constant absorbance is also obtained with 1 to 12 ml of 0.05 % TAR, 3 to 15 ml of 0.1 % ascorbic acid and 0.4 to 10 ml of ammonia buffer solutions. As ascorbic acid forms 2:1 complex with iron(II) over pH 9,6) it may act as an assistant chelating agent as well as a reducing agent to iron. The combined use of 5 ml of 1 M sodium acetate and 2 ml of 1 M sodium tartrate solutions is also possible as an assistant chelating agent. The color system follows Beer's law up to 120 μg of iron in 50 ml. The molar absorption coefficient is 2.90×10^4 l mol^{-1} cm^{-1} at 730 nm, being about 3 times as large as that of 1,10-phenanthroline. The relative standard deviation is 3.42×10^{-3} for 10 repeat determinations of 50 μg iron and the reproducibility is satisfactory. 50 μg of iron can be determined within 5 % errors in the presence of 10 mg each of 16 species, such as cadmium(II), alminum(III), chromium(III), lead(II), etc. and 1 mg each of 10 species, such as mercury(II), platinum(IV), etc. 3d type metal ions form colored complexes with TAR, but manganese(II) is tolerable up to 500 μg, and cobalt(II), nickel(II), copper(II) and zinc(II), up to 300 μg. Since the concentration of these ions in most natural water is usually low, their interferences are almost negligible. The proposed method is needless to separate iron as iron hydroxide, which needs in 1,10-phenanthroline method,7) and is possible to determine traces of iron in natural water, directly by a simple procedure. The method was successfully applied to the analysis of iron in river water of Kanazawa city, where we found 0.112 ± 0.006 ppm in Sai river(Okuwa), 0.065 ± 0.004 ppm in Tedori river(Tengu), and 0.132 ± 0.006 ppm in Asano river(Tagami). These values agreed well with those obtained by atomic absorption spectrometry.

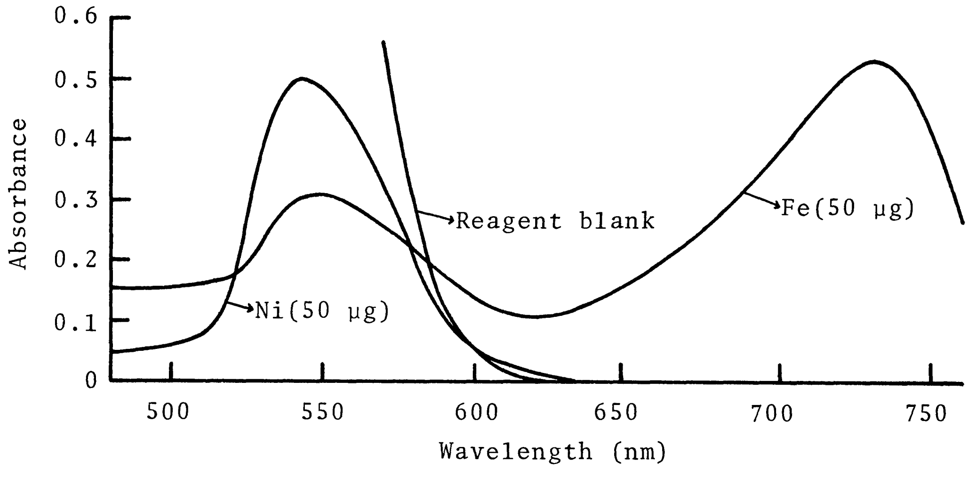

Fig. 1. Absorption spectra of TAR chelates and a reagent blank

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