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Porphyrin as a Reagent of New Indicator Reaction for the Catalytic Determination of Ultra Trace Amounts of Ruthenium(III)

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A new function of porphyrin as an analytical reagent for an indicator reaction has been developed. The decomposition rate of porphine ring with oxidizing agent was accelerated in the presence of ultra trace amounts of metal ions, such as ruthenium(III). Based on these finding, the highly selective and sensitive method for trace amounts of ruthenium(III) was developed. Its determination limit was reached down to 10^{-10} mol dm^{-3} level.

Porphyrins as a highly sensitive spectrophotometric reagent for metal ions have been demonstrated by using the Soret band ($\varepsilon = 1.5\text{-}6.5 \times 10^5$ $mol^{-1}dm^3cm^{-1}$).1-2) In spite of this excellent sensitivity, their applications to the metal ions were limited to several kinds of ones. The main reason of such limitation is due to the unusually small reaction rate of the metal ion incorporation into the porphine ring. Even though acceleration methods for the reaction, such as heating,1-2) using the metal ion exchange reaction,3-4) and adding the auxiliary ligands,5) have been proposed, no more than 10 kinds of metal ions, such as Cu, Zn, Pd, Cd, Hg, Pb, Mg, Co, Mn, and Fe were determined.1-7) Therefore, in order to apply the porphyrin to other metal ions, the development of new methods has been desired. On the course of such studies, we found that porphyrin acts as a new reagent of an indicator reaction, defined by Yatsimirskii,8) in which porphyrin was decomposed with oxidizing agent in the presence of ultra trace amounts of metal ions as catalyst, such as ruthenium(III), etc. Thus, a decrease in absorbance at the Soret band provides a highly sensitive means for detecting the catalyst metal ions. Based on this finding, highly sensitive and selective method for ruthenium(III) has been developed.

The recommended procedure of ruthenium(III) is as follows: A less than 20 cm^3 of sample solution containing 0-125 pmol ruthenium(III), is taken in a 25 cm^3 of volumetric flask, and 0.5 cm^3 of 1×10^{-4} mol dm^{-3} cobalt(III) complex solution of 5,10,15,20-tetrakis(4-sulphonatophenyl)porphine (TPPS or H_2tpps) is added. The stock solution of cobalt(III)-tpps was prepared by refluxing the mixture of TPPS and cobalt(II) in distilled water for 4 hours. In order to adjust the pH at 4.25, 2.5 cm^3 of 2 mol dm^{-3} acetate buffer solution is added. Then, 2 cm^3 of 0.25 mol dm^{-3} potassium bromate solution is added, and the mixture is diluted to the mark with water. The mixture is heated for 15 minutes in a boiling water bath. The absorbance of the reagent blank solution and that of the above mixture at the reaction time of 0 and t, given by $A_{b(0)}$, $A_{b(t)}$, $A_{s(0)}$, and $A_{s(t)}$, respectively, were measured at 426.0 nm. The concentration of ruthenium(III) is determined at t=15 min by the calibration curve of ΔA, which is given by

$$\Delta A = (A_{s(0)} - A_{s(t)}) - (A_{b(0)} - A_{b(t)}).$$

The spectral changes at the Soret band for the catalyzed and uncatalyzed reaction were observed at 20 °C as shown in Fig.1. While absorbance at the Soret band scarcely changed in the absence of ruthenium(III), it was quantitatively disappeared within 30 minutes in the presence of 1.06×10^{-6} mol dm^{-3} of ruthenium(III) ion.

This decomposition reaction was studied as follows. First, the catalytic effects of systems being in the combination of 17 kinds of metal ions and 5 kinds of redox agents were examined and the results were summarized in Table 1 .

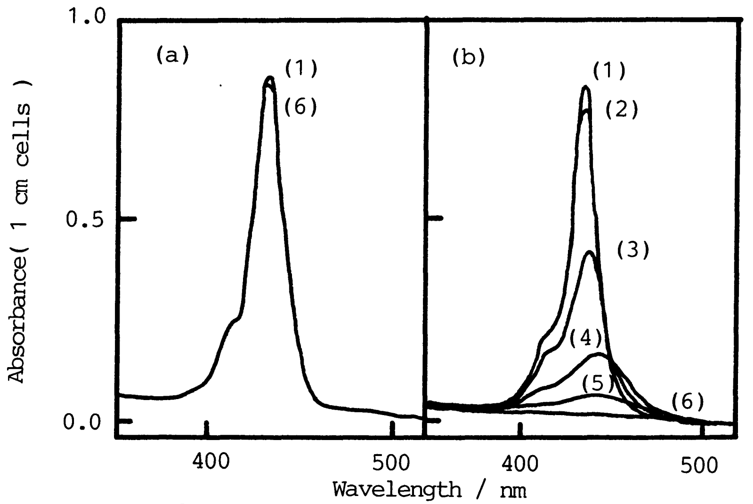

Fig.1. Spectral changes of TPPS solution by decomposition of TPPS with potassium bromate, 20 °C.

ruthenium(III) / mol dm^{-3} : (a) 0 , (b) 1.06×10^{-6}

reaction time / min : (1)0,(2)2,(3)5,(4)10,(5)15,(6)30

Table 1. Catalytic ability of metal ions for decomposition of TPPS

Redox agents	V^{V}	Cr^{III}	Mn^{II}	Fe^{II}	Co^{II}	Ni^{II}	Cu^{II}	Zn^{II}	Cd^{II}	Mo^{VI}	Au^{III}	Ru^{III}	Rh^{III}	Pd^{II}	Os^{III}	Ir^{IV}	Pt^{II}
$NaClO_3$	-	-	-	±	-	-	-	-	-	-	-	+	-	-	±	-	-
$KBrO_3$	-	-	-	±	-	-	-	-	-	-	-	++	-	-	±	-	-
KIO_3	-	-	-	-	-	-	-	-	-	-	-	±	-	-	-	-	-
H_2O_2	-	-	-	±	-	-	-	-	-	-	-	±	-	-	±	-	-
$Na_2S_2O_3$	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

pH=2.66 , Heating time : 15 min, Heating temperature : 100 °C.

Concentration of redox agents / mol dm^{-3}

$NaClO_3$: 0.01 , $KBrO_3$: 0.001 , KIO_3 : 0.02 , H_2O_2 : 0.01 , $Na_2S_2O_3$: 0.01

Order of catalytic ability : ++ > + > ± > -

The valence states of metal ions in the table indicate those in the added species. The catalytic effect was only observed for iron(II), ruthenium(III), and osmium(III) in the presence of $NaClO_3$, $KBrO_3$, KIO_3, and H_2O_2 as oxdizing agents. The catalytic effect of ruthenium(III) was remarkably large in the presence of potassium bromate, so that this combination was selected for the determination. These catalytic effects are estimated due to the outersphere electron transfer mechanism, because incorporation reactions of these metal ions into porphyrin are very slow. On the other hand, no metal ion acted as catalyst when sodium thiocyanate was used as a reducing agent.

Second, the properties of metal-porphyrin complexes, manganese(III)-, cobalt(III)-, copper(II)-, palladium(II)-, and iron(II)-tpps, as the reagent of the indicator reaction for ruthenium(III) were studied in the presence of potassium bromate. These metal-tpps complexes were prepared by usual manner. The decomposition reaction curves are shown in Fig.2. Manganese(III)-tpps was not decomposed by potassium bromate even in the presence of ruthenium(III). Further, iron(II)-tpps was easily decomposed by potassium bromate in spite of the conditions where in the absence or presence of ruthenium(III). Thus, TPPS, copper(II)-tpps, cobalt(III)-tpps and palladium(II)-tpps are the possible reagent for the indicator reaction. Ratio of apparent rate constant of the blank reaction and that of catalyzed by ruthenium(III) ion, decreased in the order of TPPS(0.0040) > palladium(II)-tpps(0.0038) > copper(II)-tpps(0.0019) > cobalt(III)-tpps(0.0014). Therefore, the highest sensitivity by the largest turn over should be expected from cobalt(III)-tpps system. And, in the case of TPPS, copper(II) and zinc(II) form their TPPS chelate rapidly, therefore these ions interfere with the reaction seriously.

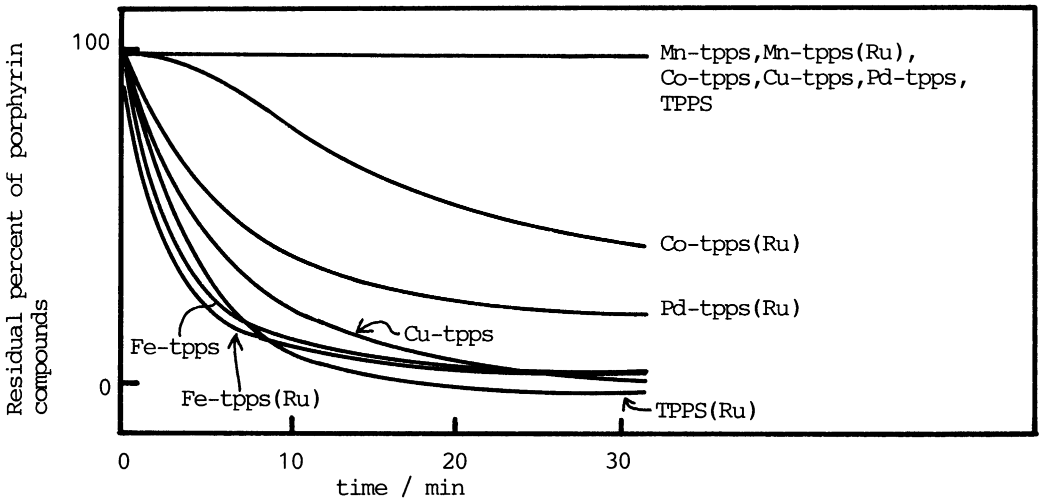

Fig.2. Decomposition reaction curves of TPPS and metal-tpps complexes. pH=4.1, at 20 °C, $[KBrO_3]_T$=0.02 mol dm^{-3}, $[TPPS]_T$ and $[M\text{-tpps}]_T$=2×10^{-6} mol dm^{-3}, and the curves with (Ru) indicates the presence of ruthenium(III) : 1.06×10^{-6} mol dm^{-3}

Based on these facts, cobalt(III)-tpps was selected as the reagent. Since the decomposition reaction of cobalt(III)-tpps at the low concentration of ruthenium(III) is very slow at room temperature, the prepared sample solution was heated for 15 minutes in the boiling water bath in order to accelerate the reaction.

The calibration curve on the range 0-5x10^{-9} mol dm^{-3} of ruthenium(III) was linear. The apparent molar absorptivity calculated from the curve was 4.74x10^{7} mol^{-1} dm^{3} cm^{-1}. This value corresponds to that one species of ruthenium turn over and decompose about 200 molecules of porphyrin within 15 minutes. The reproducibility is satisfactory and the relative standard deviation was 2.9 % for 2.66x10^{-9} mol dm^{-3} of ruthenium(III) (5 determinations). The determination limit was reached down to 1.06x10^{-10} mol dm^{-3}, which corresponded to the three times for the standard deviation of blank reaction.

The effect of diverse ions on the determination for 2.66x10^{-9} mol dm^{-3} of ruthenium(III) was examined. Iron(II), iridium(IV), and gold(III) did not interfere up to 100-fold mol of ruthenium(III), further rhodium(III), palladium(II), platinum(II), and osmium(III) did not interfere up to 1000-fold mol. This method has higher selectivity compared with the other catalytic methods of ruthenium(III).9-10)

A new application of porphyrin as a reagent for the indicator reaction provides a highly sensitive and selective method compared with the conventional metal incorporation methods. The catalytic effect of ruthenium(III) was also observed for the decomposition of another porphyrin, that is 5,10,15,20-tetrakis(N-methyl-4-pyridinio)porphine in aqueous solution and 5,10,15,20-tetraphenylporphine solubilized in micellar solution. These results suggest that the catalytic effect of ruthenium(III) may be generally seen for the oxidizing decomposition of the porphine ring. Further analytical applications of the catalytic indicator reaction with porphyrin compounds are expected for ultra trace analysis of metal ions.

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