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[Lab. of Pharm. Analytical Chemistry]

**Electrochemical Detection of Pyrroloquinoline Quinone Coupled with Its Catalytic Function by Liquid Chromatography**

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Coenzyme pyrroloquinoline quinone (PQQ) was electrochemically detected with high sensitivity and high selectivity by employing its redox catalytic function in reversed-phase HPLC. This catalytic reaction involves oxidative decarboxylation of glycine by PQQ and the reoxidation of the reduced PQQ by  $\text{Fe}(\text{CN})_6^{3-}$  to accumulate  $\text{Fe}(\text{CN})_6^{4-}$ , of which the electrochemical detection allows amplified detection of PQQ. Increase by two orders of magnitude of the current was achieved as compared with a direct reductive detection, at a reaction time of 3 min and a reaction temperature of 25 °C. The detection limit was 0.2 pmol ( $10^{-8}$  M, 20  $\mu$ l). The present method was applied to quantification of PQQ in table vinegar, milk, and swine serum.

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**Chemical and Electrochemical Investigation of Redox-Associated Conformational Changes in the Bis(1,4,7-trithiacyclononane)copper (II/I) System and X-ray Structure of the Copper (I) Complex.**

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Extensive electrochemical and X-ray crystallographic study of electron transfer in aqueous bis(1,4,7-trithiacyclononane)Cu(II) ( $\text{Cu}^{II}(\text{TTCN})_2$ ) and its Cu(I) analog have revealed that the  $\text{Cu}^{II}(\text{TTCN})_2$  system follows an ECEC square mechanism and that the uncoordinated sulfur atoms on the monodentate TTCN ligand can coordinate to a metal ion added to the solution, and this ligand ultimately converts to a tridentate ligand with the standard endodentate conformation of the TTCN moiety. Digital simulation of the cyclic voltammetric data for the kinetic parameters of the  $\text{Cu}^{II}(\text{TTCN})_2$  system and the entire mechanism of the interaction between  $\text{Cu}^I(\text{TTCN})_2$  and Cu(II) have been carried out.

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**Synthesis and Proton Transfer-Linked Redox Tuning of Ruthenium(II) Complexes with Tridentate 2,6-Bis(benzimidazol-2-yl)pyridine Ligands.**XIAO XIAOMING, MASA-AKI HAGA, TAKEKO MATSUMURA-INOUE, YU RU,  
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New Ru complexes of two tridentate ligands 2,6-bis(benzimidazol-2-yl)pyridine ( $L^1$ ) and 2,6-bis(1-methylbenzimidazol-2-yl)pyridine ( $L^2$ ) have been synthesized.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy served well for their characterization and the observed change.  $^1\text{H}$  chemical shift yields information about the electron distribution accompanying deprotonation of the ligands. The  $[\text{Ru}L^1_2]^{n+}$  chelate acts as a tetrabasic acid with  $\text{p}K_a$  ranging from 2.5 to 10.7, depending on the Ru oxidation state. The proton-coupled oxidative electron-transfer reactions of the complexes afford stable higher oxidation states such as  $\text{Ru}^{IV}$ . The properties of the complexes are discussed in comparison to those of previously reported bis(tridentate ligand)Ru compounds.