中 文 摘 要

本文综述了电致化学发光（ECL）尤其是$Ru(bpy)_3^{2+}$相关的ECL性质、机理和分析应用的研究现状和发展趋势以及抗生素的性质、检测方法、在食品中的残留问题。探索了一些抗生素对$Ru(bpy)_3^{2+}$ECL体系的影响，在此基础上建立了一系列抗生素的流动注射（FI）－ECL分析法。本论文的主要研究内容为：

基于弱碱性介质中，四环素类药物对$Ru(bpy)_3^{2+}$/TPrA的电致化学发光现象有强抑制作用。结合流动注射分析技术建立了一种电致化学发光抑制法测定四环素类药物的新方法。该法测定四环素、土霉素的线性范围分别为 2.0×10^{-8}-1.0×10^{-5} 和 1.0×10^{-8}-1.0×10^{-5} g/ml；检出限分别为 4.0×10^{-9} 和 3.8×10^{-9} g/ml。应用此FI-ECL抑制法对中成药-四环素可的松眼药膏以及蜂蜜食品中的四环素进行测定，所得结果同对照实验吻合得很好。提出其抑制机理是由于在电极表面电产生的$Ru(bpy)_3^{2+*}$ 与苯醌衍生物之间发生能量交换所致。

发现了$Ru(bpy)_3^{2+}$/TRIS/QFs体系在pH=5.0 的磷酸盐缓冲溶液中的电致化学发光现象，并与流动注射联用建立了一种测定喹诺酮类抗生素的新方法。在最优条件下，得到氧氟沙星、诺氟沙星、环丙沙星、左氧氟沙星的线性范围分别为：2×10^{-9} to 5×10^{-6}, 5×10^{-10} to 5×10^{-7}, 1×10^{-9} to 1×10^{-6}, 5×10^{-9} to 1×10^{-6}g/ml；检出限分别为：6.2×10^{-10}, 1.2×10^{-10}, 3.2×10^{-10}, 2.7×10^{-9} g/ml。并成功应用于了食品中氧氟沙星残留的测定。提出ECL反应机理是$Ru(bpy)_3^{3+}$与FQs中的仲胺和叔胺结构发生了电致化学发光反应所致，而TRIS则作为一种表面活性剂对该体系的发光具有增敏作用。

Abstract

The characteristics, mechanisms and analytical application of the electrochemiluminescence (ECL), especially $Ru(bpy)_3^{2+}$ ECL, as well as the property and analytical techniques of antibiotics and the antibiotics residues in food were reviewed in this paper. The effect of antibiotics and the antibiotics residues on $Ru(bpy)_3^{2+}$ ECL was expolored. On this basis, the FI-ECL methods were established for the determination of some antibiotics. The main results of this study are as follows:

Tetracyclines (TCs) were found to inhibite the ECL from $Ru(bpy)_3^{2+}$ / tripropylamine system when the potential of working electrode (Pt) was maintained at 1.05V (vs. Ag/AgCl) in pH 8.0 carbonate buffer solution. Based on this experimental fact, a flow injection (FI) procedure with inhibited electrochemiluminescence detection has been developed for the determination of tetracycline (TC) and oxytetracycline (OTC). Under the optimized condition, the linear range of 2.0×10^{-8} ～ 1.0×10^{-5}g/mL and 1.0×10^{-8} ～1.0×10^{-5} g/mL and the detection limit of 4.0×10^{-9} and 3.8×10^{-9} g/mL were obtained for TC and OTC, respectively. The relative standard deviations (RSD) were 0.68% and 1.18% for 5.0×10^{-7} g/mL TC and OTC (*n*=13), respectively. It was successfully applied to the determination of tetracycline in Chinese proprietary medicine- *Tetracyclini and Cortisone Eye Ointment* and the residues of tetracycline in honey products. The inhibition mechanism has been proposed due to an energy transfer between electrogenerated $Ru(bpy)_3^{2+*}$ and benzoquinone derivatives at the electrode surface.

The weak ECL of $Ru(bpy)_3^{2+}$- tris(hydroxymethyl)aminomethane (TRIS) in pH 5.0 phosphatic solution was observed. It was found that the ECL could be greatly enhanced by fluoroquinolones. On this basis, a flow injection (FI) procedure with enhanced electrochemiluminescence detection has been developed for the determination of ofloxacin, norfloxacin, ciprofloxacin and levofloxacin. Under the optimized condition, the linear range of 2×10^{-9} to 5×10^{-6}, 5×10^{-10} to 5×10^{-7}, 1×10^{-9} to 1×10^{-6}, 5×10^{-9} to 1×10^{-6}g/ml and the detection limit of 6.2×10^{-10}, 1.2×10^{-10}, 3.2×10^{-10},

2.7×10^{-9} g/ml were obtained for ofloxacin, norfloxacin, ciprofloxacin and levofloxacin, respectively. The relative standard deviations were less than 3.0%. It was successfully applied to the determination of ofloxacin residue in foods. The possible mechanism of this ECL reaction has been proposed due to that the reaction between electrogenerated $Ru(bpy)_3^{3+}$ and fluoroquninolones at the electrode surface. TRIS could enhance the ECL intensity as surfactant.