Abstract

The applications of chemiluminescence (CL) techniques in food, pharmaceutical, environmental, clinical, and other fields were reviewed. This work developed a new analytical method based on the enhancement effects of *p*-hydroxybenzoic acid and parabens on cerium(IV)-rhodamine 6G system, and applied the developed method for the determination of *p*-hydroxybenzoic acid and parabens in foodstuffs. The effects of phenol and aniline derivatives on the CL behavior of lucigenin-hydrogen peroxide-cobalt(II) system were systematically studied at different pHs, and the possible mechanism of enhancement and inhibition of lucigenin CL by the tested compounds were briefly discussed.

The more detailed information of this research work is indicated as follows:

1. The various analytical methods for the determination *p*-hydroxybenzoic acid and its esters in foodstuffs, cosmetics, and pharmaceuticals were reviewed. The advantages and disadvantages involved in the use of various techniques to determine these preservatives in the various matrices were discussed.

2. The determination of a group of parabens including methylparaben (MP), ethylparaben (EP), propylparaben (PP), and butylparaben (BP) using flow injection analysis technique with CL detection has been carried out. The method was based on the enhancement by parabens of cerium(IV)-rhodamine 6G CL in sulfuric acid medium. Under the optimized conditions, the linear range of 4.5×10^{-10}–1.5×10^{-7}, 3.0×10^{-9}–5.0×10^{-7}, 5.0×10^{-9}–1.0×10^{-6}, and 8.0×10^{-9}–8.0×10^{-7} g ml^{-1} and the detection limit of 3.4×10^{-10}, 2.0×10^{-9}, 2.0×10^{-9}, and 5.0×10^{-9} g ml^{-1} were obtained for MP, EP, PP, and BP respectively. The relative standard deviations were less than 2.0%. The method showed higher sensitivity than most of the reported methods, which also require preconcentration or derivatization. It was successfully applied to the determination of ethylparaben in soy sauces without tedious pretreatment. The possible mechanism of this CL reaction has been proposed due to that cerium(IV) was

reduced to the excited-state cerium(III) in sulfuric acid medium by the products hydrolyzed from parabens and then energy was transferred from cerium(III)* to rhodamine 6G to form the excited-state rhodamine 6G, emitting light.

3. A novel chemiluminescent method for the determination of *p*-hydroxybenzoic acid was developed, based on the enhancement by *p*-hydroxybenzoic acid of cerium(IV)-rhodamine 6G CL in sulfuric acid medium. It allowed for the detection of *p*-hydroxybenzoic acid in the concentration range 2.0×10^{-9} to 5.0×10^{-7} g ml^{-1} with a detection limit of 3.1×10^{-10} g ml^{-1}. The relative standard deviation was 1.42% (n = 11) for 1.0×10^{-8} g ml^{-1} *p*-hydroxybenzoic acid solution. The method had the merits of high sensitivity and wide linear range. It has been successfully applied to the determination of *p*-hydroxybenzoic acid in apple juice.

4. The effects of phenol and aniline derivatives on lucigenin-NaOH /$NaHCO_3$-Na_2CO_3 buffer-H_2O_2-Co^{2+} CL at different pHs have been studied. In $NaHCO_3$-Na_2CO_3 medium, some compounds enhanced the lucigenin CL while others inhibited the lucigenin CL. All tested compounds except ascorbic acid inhibited the lucigenin CL in NaOH medium. Ascorbic acid enhanced the lucigenin CL at a certain pH in NaOH medium. The magnitude of enhancement and inhibition by tested compounds was related to their molecular structure, medium, and pH. The possible mechanism of enhancement and inhibition of lucigenin CL by tested compounds were briefly discussed.

Keywords: Flow injection (FI); Chemiluminescence (CL); *p*-Hydroxybenzoic acid; Paraben (alkyl ester of *p*-hydroxybenzoic acid); Phenol and Aniline derivatives.

摘要

本文首先综述了化学发光（CL）技术在食品，医药，环境，临床以及其他领域的分析应用。基于对羟基苯甲酸和对羟基苯甲酸酯对铈（IV）－罗丹明 6G 体系的增敏作用，本文建立了新的分析方法，并将此方法应用于食品中对羟基苯甲酸和对羟基苯甲酸酯的测定；系统研究了酚胺类衍生物在不同的 pH 下对光泽精－过氧化氢－钴（II）CL 体系的影响，并讨论了其增强和抑制作用的机理。

本研究工作的详细内容如下：

1.综述了食品，化妆品和医药中对羟基苯甲酸及其酯的各种分析方法，特别是各种基质中这些防腐剂测定方法的优缺点。

2.本文基于一系列的对羟基苯甲酸酯（包括对羟基苯甲酸甲酯，对羟基苯甲酸乙酯，对羟基苯甲酸丙酯和对羟基苯甲酸丁酯）对硫酸介质中铈（IV）－罗丹明 6G化学发光体系的增敏作用，建立了它们的流动注射分析技术。在最优条件下，线性范围分别是 4.5×10^{-10}–1.5×10^{-7}, 3.0×10^{-9}–5.0×10^{-7}, 5.0×10^{-9}–1.0×10^{-6}, 和 8.0×10^{-9}–8.0×10^{-7} g ml^{-1}，检测限分别是 3.4×10^{-10}, 2.0×10^{-9}, 2.0×10^{-9}, 和 5.0×10^{-9} g ml^{-1}, 相对标准偏差都小于 2.0％。本方法比文献报道的大多数方法具有更高的灵敏度，而其他的方法还需要富集和衍生。此法已成功地应用于酱油中对羟基苯甲酸乙酯的测定，且不需要烦杂地预处理。并提出了此CL反应可能的机理：在酸性介质中，羟基苯甲酸乙酯的水解产物，将铈（IV）还原为激发态的铈（III），然后能量从激发态的铈（III）传递到罗丹明 6G，形成罗丹明 6G的激发态，从而产生CL。

3.在硫酸介质中，对羟基苯甲酸对铈（IV）－罗丹明 6G化学发光有较强的增敏作用，据此建立了流动注射化学发光测定对羟基苯甲酸的新方法。该方法灵敏度高，线性范围宽，测定对羟基苯甲酸的检出限为 3.1×10^{-10} g ml^{-1}， 方法的线性范围为 2.0×10^{-9}–5.0×10^{-7} g ml^{-1}, 对于 1.0×10^{-8} g ml^{-1}对羟基苯甲酸 11 次平行测定的相对标准偏差为 1.42％。该方法已成功地应用于苹果汁样品的分析。

4.本文系统研究了酚胺类衍生物在不同的pH下对光泽精－过氧化氢－钴（II）CL体系的影响。在$NaHCO_3$-Na_2CO_3介质中，大多数化合物对光泽精的CL有抑制作用，只有少数化合物在一定的条件下有增强作用；在NaOH介质中，除

了没食子酸外，几乎所有的化合物都呈现出抑制作用。增强和抑制作用的大小与它们的分子结构，介质，及介质的pH有关。讨论了其增强和抑制作用的机理。

关键词：流动注射（FI）；化学发光（CL）；对羟基苯甲酸；对羟基苯甲酸酯；酚胺类衍生物