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硕 士 学 位 论 文

水溶性卟啉、酞菁光学探针在酸度测定和汞(II)定量分析中的应用研究

Study on the Water-soluble Porphyrin and Phthalocyanine Optical Probes for the Detection of pH and the Quantitative Analysis of Hg(II)

杜光心

指导教师姓名：　李东辉 教授

专 业 名 称：　药 理 学

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摘 要

卟啉是一类由四个吡咯亚基的α-碳原子通过次甲基桥（=CH-）互联而形成的杂环化合物，由于其侧链的差异而形成大量衍生物，且分布广泛。卟啉分为两大类：脂溶性和水溶性卟啉化合物。后者因在水介质中有较好的溶解度长期以来在分子识别、分析化学、电化学及光化学反应等化学领域获得了广泛应用，在生物医学领域的应用也越来越令人瞩目。

血卟啉及其衍生物具有优良的光化学、光物理性质，自上世纪70年代起即作为新型光化学诊治剂得到广泛的研究与应用；其在生物医学、催化、仿生学、分析化学、环保等领域中的应用也得到逐步开拓。本论文主要研究其作为pH探针在酸度测定中的应用。

酞菁是母体结构与卟啉类似的大环类化合物，性质稳定、相对易于合成、结构可修饰性强，通过引入不同的基团可获得具有不同功能的衍生物，在高科技领域应用广泛。其中，中心配位为反磁性元素的四磺基铝酞菁（Tetrasulfonated Aluminum Phthalocyanine，AlS_4Pc）具有优良的荧光性质。该化合物具有独特的红区发射特性、量子产率高，且在水中溶解性好、光漂白作用小、光化学性质稳定，因而近年来在分析科学领域的应用研究颇为引人注目。本论文主要研究其在酸度和汞（II）测定中的应用。

本学位论文围绕水溶性卟啉和酞菁在酸度和汞（II）测定中的应用而展开，共五章。

第一章首先对卟啉和酞菁的结构、性质以及在分析科学中的应用作了简要介绍，重点阐述了卟啉和酞菁在酸度和重金属离子测定中的应用；其次，就酸度测定的研究进展做了综述，对酸度测定的意义和酸度测定方法的研究进展做了简要介绍，重点阐述了光学探针在酸度测定中的应用；最后，对测定汞的意义和测定方法的研究进展进行了综述，重点阐述了光学探针在汞测定中的应用。

第二章 利用所发现的血卟啉单甲醚对 pH 的双区间响应特性，建立了卟啉光学探针测定 pH 的新方法。研究发现，血卟啉单甲醚（Hematoporphyrin monomethyl ether ，HMME）的吸收光谱与介质 pH 的改变具有显著相关性，且呈现“双响应”特征，即 HMME 可对两个不同区间的 pH 作出响应，因而可用单

一探针实现不同区间 pH 的测定，即“一针二用”。此外，HMME 对 pH 还具有比率响应的特点。相对于强度响应探针，比率型 pH 光学探针可克服诸多非 pH 因素的影响，实现 pH 的更准确测定。本研究以血卟啉单甲醚作为 pH 新型光学探针，探索其用于小体积样品、黏稠样品以及酸度跨度较大的食品、生物样品和环境水样 pH 的测定，获得了满意的结果，显示了 pH 光学探针应用于这些检测对象的优势，开拓了光吸收型卟啉化合物在分析科学中的应用。

第三章 利用两种血卟啉类化合物对 pH 的双区间响应特性，建立荧光探针测定 pH 的新方法。研究发现，血啉甲醚（Hematoporphyrin monomethyl ether，HMME）和盐酸血卟啉（Hematoporphyrin hydrochloride，HPH）的荧光光谱与介质 pH 的改变具有显著相关性，且呈现“双响应”特征，即这两种卟啉均可对两个不同区间的 pH 作出响应。因而可用单一探针实现不同区间 pH 的荧光测定，即“一针二用”。此外，HMME 和 HPH 对 pH 还具有比率响应的特点。相对于强度响应探针，比率型 pH 荧光探针可克服诸多非 pH 因素的影响，实现 pH 的更准确测定。本研究分别以 HMME 和 HPH 两种血卟啉类化合物作为 pH 新型荧学探针，探索其用于小体积样品、黏稠样品以及环境水样 pH 的测定，获得了满意的结果，显示了 pH 荧光探针应用于这些检测对象的优势。本研究开拓了血卟啉类荧光化合物在分析科学中的应用。

第四章 基于红色荧光染料四磺基铝酞菁（Tetrasulphonated phthalocyanine, AlS_4P_C）和阿利新蓝（Alcian blue 8GX）离子对红区荧光探针在强酸性介质中的荧光增强现象，开发了一种强酸高特异性荧光分析新方法，用于检测四种常见的强酸（HNO_3、HCl、HBr、H_2SO_4）和较强酸 H_2SO_3。在最佳条件下，校准曲线的线性范围分别为：1.00-80.00 mmol/L（HNO_3），1.00-200.00 mmol/L（HCl），1.00-120.00 mmol/L（HBr），0.01-80.00 mmol/L（H_2SO_4）和 0.20-62.40 mmol/L（H_2SO_3）。检测限分别为 0.15 mmol/L（HNO_3），0.15 mmol/L（HCl），0.14 mmol/L（HBr），0.29 mmol/L（H_2SO_4）和 0.36 mmol/L（H_2SO_3）。该方法应用于人工样品的分析，结果令人满意。

第五章 基于汞（II）诱导四磺基铝酞菁（AlS_4P_C）和阿利新蓝（Alcian blue 8GX）离子对红区荧光探针的特异性荧光恢复现象，建立了汞（II）的高特异性、高灵敏的定量分析新方法。研究发现，在酸性和近中性的介质中，Alcian blue

8GX 对四磺基铝酞菁具有高效荧光猝灭作用，形成几乎无荧光的体系。而在 Hg（II）的存在下，AlS_4P_C-Alcian blue 8GX 的荧光显著恢复。进一步的金属离子筛选实验表明，只有 Hg（II）可使 AlS_4P_C-Alcian blue 8GX 体系的荧光显著恢复，而其他金属离子的存在对荧光恢复极弱或不恢复，显示 Hg^{2+}对 AlS_4P_C-Alcian blue 8GX 的响应具有高度的特异性。据此，以 AlS_4P_C-Alcian blue 8GX 构成离子对红色荧光探针，建立了 Hg（II）的高特异性、高灵敏的定量分析新方法。

关键词： 卟啉 酞菁 pH 强酸 汞（II）

Abstract

Porphyrins are macro-heterocyclic compounds formed by interconnection of α-carbon atoms of four pyrrole subunits through a methine bridge (=CH-). There are a variety of porphyrin compounds, due to the differences in the side chains. Commonly, porphyrins are divided into two classes by solubility, i.e., lipophilic porphyrins and water-soluble porphyrins. Water-soluble porphyrin has been widely used in the field of chemistry including molecular recognition, analytical chemistry, electrochemical and photochemical reactions. Their applications in bio-medical area have also attracted great attention in last decades.

Hematoporphyrin and its derivatives are well water-soluble porphyrins. They have been widely studied and applied as a new type of photochemical diagnostic reagents since 1970s, because of its excellent photochemical and photo-physical properties. In this thesis, the potential of hematoporphyrin and its derivatives as optical probes for the detection of pH or acidity was explored.

Phthalocyanines are porphyrin-like compounds containing a similar parent structure, which are physico-chemically stable, facile to be synthesized and easy to be modified in parent structure. They have been widely applied in many high-tech fields. Tetrasulfonyl aluminum phthalocyanine(AlS_4Pc), a diamagnetic metal phthalocyanine emitting strong fluorescence at red region, has been attracting more and more attention in analytical sciences, because of its good solubility in water, photo-bleaching resistance, photochemical stability, red-emitting characteristics and high quantum yield. This thesis focused on the applications of ion-paired association complex of AlS_4Pc for the determination of acidity and Hg(II).

This thesis is divided into five sections as following:

In chapter 1, the research progress of porphyrins and phthalocyanines in analytical sciences was reviewed. First, the structures, properties and applications of porphyrin and phthalocyanine, as well as their applications in analytical sciences were introduced. The main point of review focused on the applications of porphyrin and phthalocyanine in the determination of acidity and heavy metal ions.

Second, the research progress of determination of acidity was reviewed. The significance and the research progress of acidity measurement were introduced and the application of optical probes in the determination of acidity was emphasized. Finally, the progress of the determination of mercury was reviewed. The significance and the research progress of mercury measurement were introduced and the application of optical probes in the determination of acidity was emphasized.

In chapter 2, the purpose of this study is to utilize the double-interval responding characteristics to pH of an optical probe, hematoporphyrin monomethyl ether (HMME), for the establishment of a new method for the determination of pH. It was found that the absorption spectra behavior of HMME showed significant correlation with the pH of the media. Further investigation indicated that HMME could respond to two different range of pH, exhibiting a double-interval response. The study pointed out that the responding characteristics of HMME to pH could be applied to the determination of two different interval of pH by a single probe, which was a new discovery of pH optical probe. In addition, HMME was found to be a ratio responding probe, which could overcome the influence of many non pH factors, to achieve a more accurate determination of pH. HMME, as a new type of pH optical probe, has been applied to the determination of pH of trace, viscous and high acidity span samples, for example, food, biological and environmental water samples with satisfactory results. This study expends the application of porphyrin compounds in analytical sciences.

In chapter 3, fluorescent hematoporphyrin compounds (HMME and HPH), showed a double-interval responding characteristics to pH. Based on this founding, a new method for the determination of pH was established. It found that the fluorescence spectra behavior of HMME and HPH showed significant correlation with the pH of the media. Further investigation indicated that HMME and HPH could respond to two different range of pH, exhibiting a double-interval response. The study indicated that HMME and HPH could be applied to the determination of two different interval of pH by a single probe, which was a new discovery of pH

fluorescence probe. In addition, HMME and HPH were found to be a ratio responding probe, which had the advantage of overcoming the influence of many non pH factors, to achieve a more accurate determination of pH. HMME and HPH, as the new type of pH fluorescence probe, has been applied to the determination of pH of trace, viscous and high acidity span samples in this thesis with satisfactory results. This study expends the application of fluorescent porphyrin compounds in analytical sciences.

In chapter 4, a novel method for highly specific detection of strong acids based on the fluorescence recovery of the ion-paired association complex, tetrasulfonated aluminum phthalocyanine (AlS_4Pc)-Alcian blue 8GX, which emits at long wavelength was constructed. Under the optimal conditions, the linear range of the calibration curves were 1.00-80.00 mmol/L (HNO_3), 1.00-200.00 mmol/L (HCl), 1.00-120.00 mmol/L (HBr), 0.01-80.00 mmol/L (H_2SO_4), and 0.20-62.40 mmol/L (H_2SO_3), respectively. The detection limits were 0.15 mmol/L (HNO_3), 0.15 mmol/L (HCl), 0.14 mmol/L (HBr), 0.29 mmol/L (H_2SO_4) and 0.36 mmol/L (H_2SO_3), respectively. The present method has been applied to the analysis of artificial samples with satisfactory results.

In chapter 5, it was found that the fluorescence of AlS_4Pc was dramatically quenched by Alcian blue 8GX because of the formation of non-fluorescent association complex (AlS_4Pc-Alcian blue 8GX). However, fluorescence of the complex recovered obviously in the presence of Hg(II) in acidic or near neutral media. Screening experiments on common metal ions revealed that only Hg(II) could significantly restored the fluorescence of the complex, while the presence of other metal ions was weak or not restored fluorescence, indicating the high specificity of the response to Hg(II) of AlS_4Pc-Alcian blue 8GX. Based on these foundings, a highly specific and sensitivity method for quantitative analysis of mercury (II) ions was proposed.

Keywords: Porphyrin; phthalocyanine; pH ;strong acid; Hg^{2+}

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