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## 摘要

近年来的研究表明,元素的不同形态与其物理化学性质和环境行为及生物效应密切相关。联用技术已经成为元素形态分析中应用最广泛的技术,而高效液相色谱(HPLC)和原子荧光光谱(AFS)通过高效的在线接口链接联合使用由于其简便、灵敏度高、选择性强、经济实用等优点已经被越来越多地应用于可蒸气发生元素的形态分析。常用的蒸气发生进样方法采用硼氢化钾/氢氧化钠-盐酸( $\text{KBH}_4/\text{NaOH-HCl}$ )体系,此体系进样效率高,但是也具有以下缺点:(1)  $\text{KBH}_4$ 不稳定,要现配现用;同时由于其不稳定,制备高纯的  $\text{KBH}_4$  相对困难,它的使用常常引入杂质并使背景升高;(2) 易受共存离子特别是过渡金属离子的干扰;(3) 产生的大量氢气会降低等离子体的稳定性甚至熄灭等离子体;(4) 对样品中待测元素的氧化还原状态要求苛刻。发展高效的还原蒸气进样体系可以克服上述传统  $\text{KBH}_4/\text{KOH-HCl}$  体系的不足。

汞是一种典型的有毒金属元素,对人体的毒害作用早已被报道。汞进入人体内可以和各种物质结合,而有机汞因其亲脂性具有更强的毒性。本硕士学位论文发展了光催化还原汞的新体系,设计制作了相应的光催化装置作为 HPLC 和 AFS 的新接口,并应用于环境生物样品中汞的形态分析。

本论文的主要贡献是 1) 首次利用溶胶-凝胶法在玻璃纤维表面修饰了纳米  $\text{TiO}_2$  薄膜,利用其在紫外光(UV)的辐射下可产生电子( $\text{e}^-$ )和空穴( $\text{h}^+$ )的机制,使用  $\text{h}^+$  捕获剂湮灭  $\text{h}^+$ ,从而利用在反应体系中获得的自由  $\text{e}^-$  对汞的各种形态进行还原;设计制作了光催化反应装置作为 HPLC 和 AFS 的接口并成功应用于环境生物样品中汞的形态分析。2) 首次建立了基于 UV 辐射-巯基乙醇(ME)还原汞的新体系,研究了其可能的光催化还原机理,并作为 AFS 测定汞形态的蒸气发生进样的新方法应用于汞的形态分析。本论文包含以下几个部分:

第一章主要对汞在自然界中的含量和存在状态进行了阐述,解释了汞形态分析工作的重要性和现实意义,对汞形态分析中采用的各种联用技术方法进行了详细的介绍。对常用蒸气发生  $\text{KBH}_4/\text{KOH-HCl}$  体系的优缺点进行分析,并提出发展新的汞还原体系用于链接 HPLC 和 AFS 的接口的设想。

第二章发展了离子对高效液相色谱分离,纳米  $\text{TiO}_2$  光催化在线还原,原子

荧光光谱检测的新体系，并用此体系分离检测了无机汞、氯化甲基汞、氯化乙基汞和氯化苯基汞；对半导体纳米  $\text{TiO}_2$  光催化的相关理论进行阐述，优化了制备纳米  $\text{TiO}_2$  薄膜的反应温度、溶胶 pH、热处理温度等条件，采用水热处理消除薄膜表面的龟裂。BCR 标准参考物 BCR463（金枪鱼）和 BCR580（河口底泥）被用来验证所建立的汞形态分析方法的准确度，最后将其应用于实际海产样品和底泥样品汞的形态分析。

第三章建立了 UV/ME 光催化还原新体系，利用 FT-IR 和 GC-MS 对其可能的的光催化还原机制进行了探讨，作为新型的汞冷蒸气发生的高效液相色谱和原子荧光光谱联用的接口技术实现了甲基汞和无机汞两种形态的测定。

第四章总结了本硕士研究论文的研究工作，对其存在的不足进行了检讨，对进一步开展研究工作进行了展望。

关键词：汞形态分析 高效液相色谱—原子荧光光谱联用技术 纳米  $\text{TiO}_2$  光催化 2-巯基乙醇光催化还原

## Abstract

Recent approaches indicated that the environmental behavior and biological function as well as physicochemical property of an element depend mainly on the kind of its existing species. Hyphenated techniques combining a continuing separation technique and an element-selective and/or a structure-specific detector play an important role in elemental speciation analysis. Among these, effectively bridging both of separation and detection is a crucial for achieving a successful job. Chemical vapor generation as an effective sample introduction method in atomic spectrometry was used frequently for the determination of vapor generable elements, for example, traditional  $\text{KBH}_4/\text{KOH-HCl}$  system, but some drawbacks should be also noted that (1)  $\text{KBH}_4$  is very unstable and also a potential source of contamination, it must be prepared daily in alkaline solution; (2) susceptibility to interferences from common transition metals; (3) large amount of hydrogen generated during the decomposition of  $\text{KBH}_4$  reduces the stability of the plasma or even extinguishes the plasma; (4) difficult to convert the species of an element existing in high oxidation state or as organic complex into volatile species. It is necessary to develop new vapor generation systems and overcome the disadvantages mentioned above.

Mercury is ubiquitous in the environment and thus a most extensively studied element because of its extreme toxicity, especially in its organic form. In this thesis, new photocatalytic reduction systems have been developed and the corresponding devices were designed to be used as interfaces between high performance liquid chromatography (HPLC) and atomic fluorescence spectrometry (AFS) for Hg speciation analysis. The established methods were successfully applied to the determination of Hg species in environmental and biological samples.

This main contributions of this thesis are that i) fabricating a novel UV/ $\text{TiO}_2$  photocatalysis reduction device (UV/ $\text{TiO}_2$  PCRD) by modifying nano  $\text{TiO}_2$  film onto a glass fibre. Hg species were reduced into the so-called cold vapor by the free electrons ( $e^-$ ) generated on the surface of the  $\text{TiO}_2$  when it was irradiated by UV and a

hole ( $h^+$ ) scavenger was used. It was used as an interface between HPLC and AFS for Hg speciation in environmental and biological samples. ii) developing a new photocatalytical reduction system based on mercaptoethanol radical mechanism under UV irradiation for Hg determination and speciation analysis by AFS and HPLC-AFS. This thesis consists of 4 chapters as below:

In Chapter One, the abundance and existing species of Hg in the environment as well as its toxicity was briefly introduced; the current status of Hg determination and speciation has been reviewed briefly including the sample pretreatment, separation and detection techniques and the interface between them as well. Research proposal was thus made for this thesis, aiming to develop new photocatalytical reduction systems as on-line interfaces to couple HPLC and AFS for Hg determination and speciation including UV/TiO<sub>2</sub>-PCR and UV/ME systems.

In Chapter Two, an introduction to nano TiO<sub>2</sub> photocatalysis has been presented, and then TiO<sub>2</sub> photocatalytical reduction system for Hg species was developed firstly; the possible mechanism was discussed. The UV/TiO<sub>2</sub> PCR was used as an interface between ion-pair HPLC and AFS for the four common Hg species including inorganic mercury (Hg<sup>2+</sup>), methyl mercury chloride (MMC), ethyl mercury chloride (EMC) and phenyl mercury chloride (PMC). We also optimized the reaction temperature of nano TiO<sub>2</sub> film preparation, pH of the sol, the temperature of the calcination and adopted hydrothermal treatment to clean up the cracks of the film. Furthermore, BCR certified reference materials (BCR 463 tuna fish and BCR 580 estuarine sediment) was used to validate this new method, and it was finally applied to the speciation of Hg species in real shell fish samples collected around Xiamen Island and lake sediment sampled on Xiamen Island.

In Chapter Three, a new vapor generation system for Hg species was developed and used as a sample introduction unit before AFS determination. It was validated by the BCR CRMs and applied to the determination of total Hg and methyl Hg in seafood and sediment samples collected around and/or on Xiamen Island. Moreover, the possible photocatalytical reduction mechanism of UV/ME to Hg was studied and proposed based on the evidences from FT-IR and GC-MS experiments, being that the

photocatalytical reduction follows free radical mechanism.

In Chapter Four, a summary of this thesis was concluded and the developing trend was also discussed.

Keywords: HPLC-AFS; nano TiO<sub>2</sub>; mercury species; mercaptoethanol

厦门大学博硕士学位论文摘要库



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## 第一章 前言

### 1.1 汞的概述

汞是一种毒性较大的有色金属，俗称水银。在常温下是发光的银白色液体，是室温下唯一的液体金属。汞的熔点低，为 $-38.87^{\circ}\text{C}$ ，在 $356.95^{\circ}\text{C}$ 沸腾。汞在熔化时，即开始有蒸发，故在 $0^{\circ}\text{C}$ 就有一定的汞蒸气，温度越高，蒸气越多。在 $20^{\circ}\text{C}$ 时，汞蒸气压是 $0.0013$ 毫米汞柱，因此具有较大的挥发性。汞的比重是 $13.546$ （ $20^{\circ}\text{C}$ 时），其蒸气密度是空气的 $7$ 倍，由于汞的表面张力很大，易形成小滴而沉积<sup>[1]</sup>。汞是比较稳定的金属，在室温下不被空气氧化，也不与盐酸和稀硫酸作用，但汞与硫的结合能力较大，与硫磺混合即能形成硫化汞（ $\text{HgS}$ ）。汞被广泛应用于工业、农业、科学技术、交通运输、医药卫生以及军工业生产等领域<sup>[2]</sup>。

汞在地壳中的总储量达 $1600$ 亿吨，地壳中的含量为 $0.01\sim 20\text{ mg/kg}$ ，但整个地壳中的汞有 $99.98\%$ 成稀疏的分散状态，只有 $0.02\%$ 富集于可以开采的矿床中。即汞微量但广泛地分布在岩石、土壤、大气、水和生物之中，构成地球化学循环。汞在全球的分布从地图上看是呈盘边型状，主要由三个宽的汞矿带构成，一条是从南美南部沿着南美、中北美西部到美国的阿拉斯加，再向西到东北亚交于日本北部；第二条是呈弓型状通过日本、菲律宾、印度尼西亚到新西兰和澳大利亚东部；第三条是沿喜马拉雅山和阿尔卑斯山汞矿带到西班牙。地壳中汞含量平均为 $77\text{ ng g}^{-1}$ ，火成岩的平均含汞量为 $0.08\text{ mg kg}^{-1}$ ，海水含汞量为 $10\sim 300\text{ ng L}^{-1}$ ，世界土壤的平均含汞量为 $0.03\sim 0.1\text{ mg kg}^{-1}$ ，而我国土壤中汞的背景值在 $0.02\sim 0.19\text{ mg kg}^{-1}$ 之间<sup>[3]</sup>。

19世纪以来，随着工业的发展，汞的用途越来越广，生产量急剧增加，从而使大量汞由于人类活动而进入环境。Nriagu和Pancyna<sup>[4]</sup>估计全球范围内每年释放到大气的总汞量达 $7500\text{ t}$ ，其中因人为过程排放到大气的汞为 $3500\text{ t}$ ，经自然释放为 $3000\text{ t}$ 。在人为排放源中，化石燃料燃烧是最主要的部分。

#### 1.1.1 环境中的汞<sup>[5]</sup>

大气中的汞含量为  $0.009\sim 38\text{ ng/m}^3$ 。由于汞具有独特的大气远距离传输特征，被公认为全球性的污染物。据估计，全球地表每年释放到大气的总汞量约为  $6000\sim 7500\text{ t}$ ，其中  $50\%\sim 75\%$  以上源于人为活动途径。散发到大气中的汞经过一定距离的传输，大约有  $93.7\%$  回降于陆地。

海水中汞的污染暴露浓度一般为  $0.03\sim 2.00\mu\text{g/L}$ ，江、河和湖泊为  $0.07\mu\text{g/L}$ ，但泉水中汞污染暴露一般可达  $80\mu\text{g/L}$  以上。各种工业排放的含汞废水成为水体中汞污染暴露的主要途径与来源。施用含汞农药和含汞污泥肥料及污水灌溉成为土壤中汞污染暴露的主要途径与来源。

目前，土壤中汞的污染暴露自然水平一般为  $0.01\sim 0.80\text{ mg/kg}$ ，与地壳中汞的丰度相当。各种由于风化、地震、火山爆发以及生物转化等因素，促使汞在环境中具有本底含量，而人类活动使汞的含量在这些本底水平的基础上又有增加。

环境中的汞的转化代谢途径如图 1-1 和 1-2 所示。

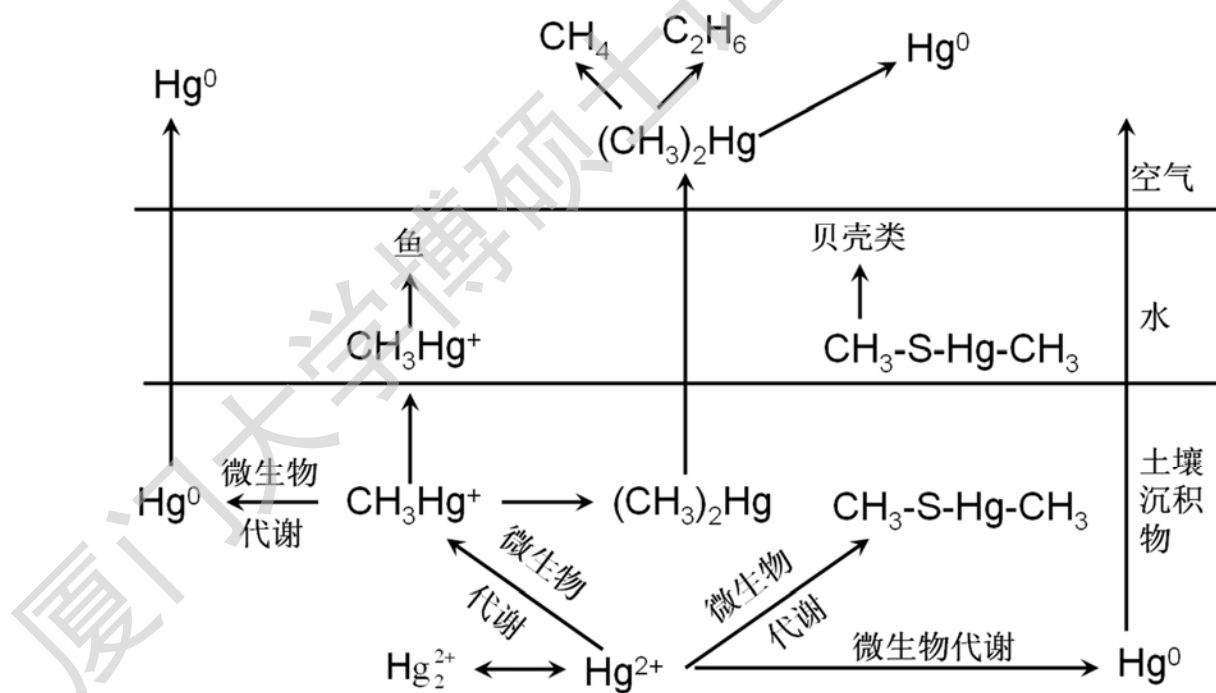


Fig 1-1 The transformation of mercury species in food chain<sup>[8]</sup>

图 1-1 汞形态在食物链中的转化图<sup>[8]</sup>



Degree papers are in the "[Xiamen University Electronic Theses and Dissertations Database](#)". Full texts are available in the following ways:

1. If your library is a CALIS member libraries, please log on <http://etd.calis.edu.cn/> and submit requests online, or consult the interlibrary loan department in your library.
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