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硕 士 学 位 论 文

海洋环境样品中汞和甲基汞
原子荧光测定方法的建立、验证及应用

Validation and Application of Analytical Methods for
Determination of Total Mercury and Methyl Mercury
In Marine Environmental Samples

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厦门大学博硕士学位论文摘要

摘 要

汞是一种可在全球循环的持久性有毒污染物，人类活动是汞污染的主要成因。各形态的汞化合物中，无机汞较容易排泄，而有机汞毒性较强，其中甲基汞毒性最大。为研究环境中汞的含量、分布及形态，进而探讨汞污染来源、汞的环境行为和生态毒理效应，各种环境样品中汞和甲基汞的分析方法不断发展。

然而，我国测定总汞、甲基汞的现行标准方法仍存在不足。对于总汞测定，针对海洋环境样品的 GB17378.6-2007 国家标准方法无法满足海水样品中低浓度汞的测定需要；冷原子吸收光度法装置复杂，不便普及应用。因此，建立统一的海水、生物体和沉积物中汞分析的方法，以便于进行数据统计和比对分析是十分必要的。

目前，甲基汞的测定仅在全国为数不多的几个实验室实现，且国家标准单一，未有专门针对海洋环境样品的标准方法；国家标准 GB/T 17132-1997 所采用的气相色谱法前处理过程繁琐，装置复杂，较难学习掌握；有机试剂毒性较强，对实验者和环境有一定影响。

因此，对海洋环境样品中汞和甲基汞的分析方法进行完善和验证是十分紧迫的。本论文依托国家海洋局海洋公益性行业科研专项课题：近海重金属污染新型监测与风险评估技术业务化示范应用（201105015），参考国际普遍认可的汞、甲基汞测定方法，结合我国海洋研究单位和监测站的实际情况，以方法检测限低、设备简单易得、成本适中、便于普及应用为目标，建立并验证了汞和甲基汞的原子荧光测定方法，成功开展了实验室互校工作，并将建立的测定方法应用于泉州深沪湾水环境中汞和甲基汞的分布研究。论文主要内容及结果如下：

（1）建立和验证了海洋环境样品中总汞的氧化-吹扫-金柱捕集-热脱附（双柱）-冷原子荧光光谱法。在优化的实验条件下，方法具有良好的重现性和灵敏度，测定海水的方法检测限（Method Detection Limit, MDL）为 0.63 ng/L，测定土壤、沉积物等固体样品的 MDL 为 0.14 ng/g。各项质量控制数据达标，沉积物标准参考物质（Standard Reference Material, SRM）的测定值为 $0.082 \pm 0.004 \mu\text{g/g}$ ，与保证值（ $0.078 \pm 0.006 \mu\text{g/g}$ ）相符。本方法适用于不同海洋环境样品中总汞浓

度的测定，特别适用于复杂基底样品，例如海水中低含量总汞的测定。

(2) 成功建立和验证了海洋环境样品中甲基汞的乙基化-气相色谱分离-原子荧光光谱法。在优化的实验条件下，方法的重现性和灵敏度良好，测定海水的 MDL 为 0.076 ng/L (以汞计)，测定沉积物样品的 MDL 为 0.021 ng/g (以汞计)，测定生物样品的 MDL 为 0.013 ng/g (以汞计)。各项质量控制数据达标，鱼肉 SRM 的测定值为 $0.83 \pm 0.03 \mu\text{g/g}$ ，与保证值 ($0.84 \pm 0.03 \mu\text{g/g}$) 相符。本方法灵敏可靠，适用于不同海洋环境样品中甲基汞的常规监测，特别适用于海水中低含量甲基汞的测定。

(3) 利用建立的近海海水、沉积物、生物样中总汞、甲基汞的测定方法，参与总汞、甲基汞方法的实验室互校工作。结果表明，各实验室所获数据具有一致性和可比性。实验操作简便易行，可在短期内掌握，适于普及应用。该方法将收录在《近海重金属污染新型监测技术规程》中。

(4) 应用建立的总汞、甲基汞测定方法，测定了采集自福建省泉州市深沪湾 8 个海水样、8 个沉积物和 33 个生物样中的总汞和甲基汞。海水总汞浓度范围为 1.16~7.29 ng/L，平均值为 3.32 ng/L。沉积物中总汞浓度范围为 0.006~0.066 $\mu\text{g/g}$ ，甲基汞占总汞的比例为 4.7%~38.6%，该比例与总汞浓度呈负相关关系 ($r=-0.840, p<0.05$)，这可能是因为总汞浓度的升高使甲基汞合成反应受到抑制，导致反应速率降低甚至为负。生物样中总汞浓度的范围为 0.037~0.353 $\mu\text{g/g(dw)}$ ，甲基汞范围为 1.01~42.5 ng/g (dw)，甲基汞占总汞的比例为 1.5%~40.4%。甲基汞浓度与总汞浓度显著相关 ($r=0.484, p<0.1$)，甲基汞占总汞比例与总汞浓度略有负相关 ($r=-0.293, p<0.1$)。因此可以推测，生物中的总汞和甲基汞都是外源性的，生物体吸收甲基汞的速率略低于吸收总汞的速率。以美国 EPA 规定的甲基汞参考计量 (RfD) 0.1 $\mu\text{g}/(\text{kg}\cdot\text{d})$ 为标准，对深沪湾居民进行海产品摄入量评估，认为深沪湾周边居民每周食用 3 次湾内的海产品是安全的。

关键词：总汞；甲基汞；原子荧光光谱法；方法验证；深沪湾；分布

ABSTRACT

Mercury is a persistent toxic pollutant cycling around the world. Anthropogenic activity is the main source of mercury pollution. Among all mercury species, inorganic mercury is easier to excrete, while organic mercury is more toxic. Methyl mercury is considered to be the most toxic organic mercury. To better understand the distribution, speciation, behavior and toxicity of mercury, the analytical methods of various environmental samples have been developing.

The standard methods for mercury determination need further improvement in China. For analysis of total mercury (THg), the active national standard method GB17378.6-2007 that targets marine environmental samples can not meet the needs of determination of low concentration mercury in seawater. Moreover, the cold vapor atomic adsorption spectrometer can not appeal to most of the experimenter due to its complicate device. Therefore, it is necessary to develop unified methods of determination of mercury in seawater, sediment and biota, to provide standardized data for statistic analysis and comparison.

Currently, methyl mercury (MeHg) determination can only be fulfilled in a few labs in China. There is still lack of standard methods for determination of methyl mercury in marine environmental samples. The only current national standard method GB/T 17132-1997 adopts gas chromatography to determine methyl mercury in various samples. However, it is relatively hard to master for its labor-intensive pretreatment process and complicate device. Even more, the organic reagents used in extraction steps are harmful to experimenter and nearby environment.

Therefore, it is imperative to establish and validate analytical methods for determination of THg and MeHg in marine environmental samples. This research is based on a public oceanic welfare project issued by State Oceanic Administration of China. By referring to the methods of mercury determination approved international wide, together with the consideration of practical situation of marine research and monitoring institutes, this research was aimed to establish and validate methods for determination of THg and MeHg, which were supposed to be low in detection limit,

simple in device, moderate in cost and easy in application. Furthermore, the intercomparison of the established analytical methods among laboratories has been carried out, and the methods have been applied to investigate distribution of THg and MeHg in Shenhu Bay, Quanzhou. The main contents of this research are as follows:

(1) The method of THg determination with oxidation, purge and trap, thermal desorption (dual amalgamation) and cold vapor atomic fluorescence spectrometer (CVAFS) has been established and validated. With the optimized conditions, the method had good reproducibility and sensitivity. The method detection limits (MDL) for seawater, biological and sediment samples were 0.63 ng/L, 0.14 ng/g and 0.14 ng/g, respectively. Data of quality control were acceptable. The analytical result of a sediment standard reference material (SRM) was 0.082 ± 0.004 $\mu\text{g/g}$, consisting with the certified value (0.078 ± 0.006 $\mu\text{g/g}$). The proposed method is suitable for routine determination of THg in different marine samples, especially for analyzing low-level THg in complicated matrix, such as in seawater.

(2) The method of MeHg determination with ethylation, GC separation and CVAFS has been established and validated. With the optimized conditions, the method had good reproducibility and sensitivity. The MDLs were 0.076 ng/L, 0.013 ng/g and 0.021 ng/g (expressed as Hg) for seawater, biological and sediment samples, respectively. Data of quality control were acceptable, and the analytical result of fish SRM was 0.83 ± 0.03 $\mu\text{g/g}$, which was comparable with the certified value of 0.84 ± 0.03 $\mu\text{g/g}$. The method is sensitive, reliable for the routine determination of MeHg in different marine samples, and especially suitable for analyzing low-level MeHg in seawater.

(3) The intercomparison of the analytical methods mentioned above among laboratories has been carried out. The results show that the methods could provide comparable data among laboratories. The experimental operation can be easily handled and mastered quickly, indicating the practicability of the methods. Furthermore, the methods will finally be included in the Technical Regulation of Heavy Metal Pollutants in Coastal Areas.

(4) The methods described above have been applied to determine THg and MeHg

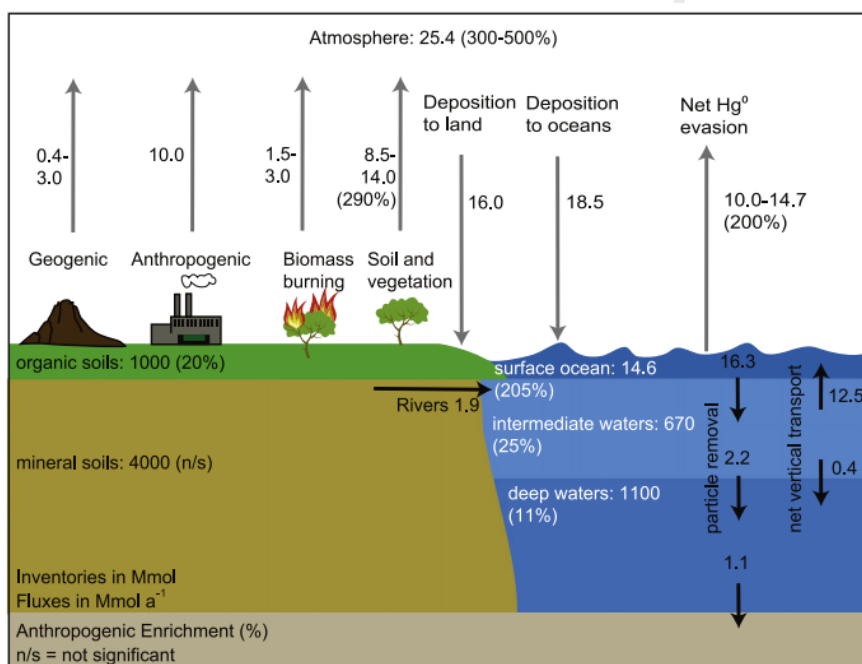
in eight seawater samples, eight sediment samples and thirty three fish samples collected from Shenhui Bay. THg concentrations in seawater ranged from 1.16 ng/L to 7.29 ng/L with an average of 3.32 ng/L. The concentrations of THg in sediment were between 0.006 and 0.066 $\mu\text{g/g}$, with MeHg contributing 4.7%~38.6% of THg. The concentrations of THg in sediment were negatively correlated ($r=-0.840$, $p<0.05$) with the percentage of MeHg, suggesting that higher THg concentrations led to lower, even negative methylation rates. Analytical results of biota samples showed that THg concentrations ranged between 0.037~0.353 $\mu\text{g/g}$ (dw), and MeHg 1.01~42.5 ng/g (dw), with MeHg accounting for 1.5%~40.4%. Moreover, the concentrations of THg and MeHg were significantly correlated ($r=0.484$, $p<0.1$), while the percentage of MeHg was negatively correlated ($r=-0.293$, $p<0.1$) with the concentration of THg. Therefore, it was speculated that THg and MeHg in biota were extraneous. The uptake rate of MeHg was slightly lower than that of THg. Based on the MeHg Reference Dose (RfD) of 0.1 $\mu\text{g}/(\text{kg}\cdot\text{d})$ regulated by U.S.EPA, estimation for human consumption of residents in Shenhui Bay has been assessed. Results showed that it would be safe to consume 600 g fish per week from Shenhui Bay.

Key words: total mercury; methyl mercury; cold vapor atomic fluorescence spectrometry; validation; Shenhui Bay; distribution

第1章 绪论

1.1 汞的污染来源及循环

汞是一种持久性有毒污染物^[1]，对人类及其他生物有严重的危害。汞又是一种可以气态化合物形态存在的污染物，因此其更易在各环境介质和全球循环。图 1-1 和图 1-2^[2]描述了汞和甲基汞在自然界中的主要循环过程。为了对汞循环进行定量研究，科学家利用已掌握的大量数据，建立多种数学模型，如 GEOS-Chem 模型，对汞在各界面间的通量进行估算^[2]。



注：括号中的百分数代表上世纪由于人类活动引起的汞浓度增量

图 1-1 利用 GEOS-Chem 模型计算的地表总汞通量^[2]

Fig. 1-1 A recent estimate of the fluxes of mercury at the Earth's surface based on simulations using the GEOS-Chem global mercury model^[2]

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