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博 士 学 位 论 文

海水中痕量元素含量及其在不同分子量段  
DOM 上分布的测定方法研究与理论初探  
Measurement and Preliminary Theoretical Study of Trace  
Element Concentration and Their Distributions on Different  
Molecular DOM in Seawater

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## 摘要

痕量元素的含量及其分布在海洋生态系统、海洋环境变化等方面具有关键性的作用。由于海水中金属元素浓度处于痕量水平或更低，加之海水基体复杂，存在仪器灵敏度不足、采样及样品分析过程易玷污等问题，常使用共沉淀、液液萃取、螯合树脂等前处理手段，但这些方法操作复杂、试剂使用量大、方法空白高，很大程度上制约了研究的深入开展。故建立一些准确、方法空白低、精密性好的痕量元素含量及其赋存分布的测定方法，具有重要的海洋学意义。

本研究将聚合物络合超滤技术引入到海水痕量元素分析，利用聚合物对海水中目标元素选择性的络合，实现了基体分离及目标物的富集，随后使用电感耦合等离子体质谱（Inductively coupled plasma mass spectrometry, ICP-MS）进行准确测定，建立了聚合物络合超滤分离富集-ICP-MS 测定海水中多种痕量元素含量的方法。另外，对海水中痕量元素的化学平衡模型理论进行初探，分别对凝胶色谱-电感耦合等离子体质谱联用技术和离心超滤技术进行研究，通过建立模型计算得到聚乙烯亚胺-金属络合物的稳定常数，并建立了海水中不同分子量段溶解有机物（Dissolved organic matter, DOM）上痕量元素赋存分布的测定方法，为海水中痕量元素的含量、分布、迁移、转化等海洋地球化学过程的探讨提供技术支撑与理论基础。研究内容主要分为以下 4 个部分：

(1) 建立了聚乙烯亚胺（Polyethyleneimine, PEI）络合-超滤分离富集-电感耦合等离子体质谱分析海水中 6 种痕量金属元素的方法。室温条件下，当 PEI 浓度高于 20 mg/L、反应时间大于 25 min、pH 大于 7.5 时，海水中的  $\text{Cu}^{2+}$ 、 $\text{Pb}^{2+}$ 、 $\text{Cd}^{2+}$ 、 $\text{Co}^{2+}$ 、 $\text{Ni}^{2+}$  等金属离子与 PEI 形成络合物，经超滤截留在滤膜后，用 2.5 mL 3.0% (v/v) 的  $\text{HNO}_3$  进行解离，实现金属离子从海水中定量分离、富集。分离富集后的金属元素使用 ICP-MS 的全定量数据采集模式、内标校正的标准校正曲线法进行定量分析。方法的相对标准偏差（RSD）在 3.4%（Cd）~9.3%（Pb）之间（0.20  $\mu\text{g/L}$ ,  $n=5$ ），标准加入回收率为 78.7%（Ag）~95.2%（Cu）；方法的检出限（LODs,  $10\sigma$ ）为 1.2 ng/L（Cd）~9.8（Cu）ng/L，方法空白极低，均低于检出限。建立的方法可应用于近岸及河口海水样品中 6 种痕量金属元素的同时测定。

(2) 建立了聚丙烯酸 (Poly-acrylic acid, PAA) 络合-超滤分离富集-电感耦合等离子体质谱测定海水中 24 种痕量稀土及金属元素的方法。pH 大于 7.5 时, 海水中的稀土离子、 $\text{Cu}^{2+}$ 、 $\text{Pb}^{2+}$ 、 $\text{Cd}^{2+}$ 、 $\text{Co}^{2+}$ 、 $\text{Ni}^{2+}$  等与 PAA 形成稳定的络合物, 经超滤截留、 $\text{HNO}_3$  解离后, 实现稀土及金属元素从海水中分离、富集; 分离富集后的待测元素用 ICP-MS 的全定量数据采集模式、内标校正的标准校正曲线法进行定量分析。优化实验条件下, 方法的相对标准偏差 (RSD) 在 1.74% (Cd) ~ 7.34% (Eu) 之间 ( $0.02 \mu\text{g/L} \sim 0.10 \mu\text{g/L}$ ,  $n=5$ ), 标准加入回收率为 72.8% (Ag) ~ 95.8% (Sm); 方法的检出限 (LODs,  $10\sigma$ ) 为  $0.23 \text{ ng/L}$  (Ho) ~  $12.85 \text{ ng/L}$  (Pb), 方法空白均低于检出限。建立的方法可应用于近岸及河口海水中痕量稀土及金属元素的同时测定。

(3) 对海水中痕量元素的化学平衡模型理论进行了初探, 以此作为海水中元素赋存形态研究的理论基础。建立了凝胶色谱柱-电感耦合等离子体质谱联用体系 (GPC-ICP-MS) 测定并计算得到聚乙烯亚胺-金属 (PEI-M) 络合物的络合稳定常数 ( $K$ ) 与平均配位数 ( $n$ ) 的方法。配制不同浓度的 PEI 和  $\text{M}^{2+}$  的混合溶液, 振荡溶液至反应平衡后, 经 GPC-ICP-MS 对  $\text{M}^{2+}$  和 PEI-M 进行分离测定。最后通过简单的络合物化学理论模型, 计算得到 PEI-M 的络合稳定常数与平均配位数。pH 为 4.1~5.3 时, PEI-Cu 的络合稳定常数为 8.7~9.7, 平均配位数为 1.0~1.3; PEI-Cd 的络合稳定常数为 9.7~10.7, 平均配位数为 1.0~1.3。pH 4.1~5.3 时, PEI-Cu 和 PEI-Cd 合稳定常数随着 pH 增大而增大。主要是因为随着 pH 的增大, PEI 中胺基的质子化程度降低, PEI 与  $\text{M}^{2+}$  的络合能力增强, 相应的络合稳定常数增大。该方法测定的  $K$  和  $n$  能为 PEI 络合分离水体中  $\text{M}^{2+}$  的条件提供理论预测。

(4) 建立了离心超滤分离富集-电感耦合等离子体质谱 (UF-ICP-MS) 联用体系, 测定近岸及河口海水中痕量元素在不同分子量段 DOM 配体中的天然赋存分布。该方法具有灵敏度高、空白低、多样品同时处理、多元素同时测定等优点, 运用所建方法对九龙江河口区海水样品进行了测定, 发现海水中元素在不同分子量段 DOM 上的分布存在较大的差异。随着盐度的增加, DOC 浓度逐步降低, 海水中高分子量的 DOM 减少, 各元素的总体浓度呈降低趋势。而赋存在不同分子量 DOM 上的各个元素, 并非都随着盐度的增大呈现递减的趋势。海洋学研究中的颗粒活性元素 (如 Th、Pb 等) 主要分布于高分子量段的 DOM 上 ( $100 \text{ kD} \sim$

0.45  $\mu\text{m}$ ), 中间分子量段的 DOM 也能络合一定量的元素, 低分子量段 ( $<5$  kD) 分布最少; 对于非颗粒活性元素 (如 Co、Ni、Ag 等), 其主要赋存于低分子量段的 DOM 上 ( $<5$  kD), 高分子量段的 DOM (300 kD $\sim$ 1000 kD 与 1000 kD $\sim$ 0.45  $\mu\text{m}$ ) 也能络合一定量的元素, 中间分子量段的 DOM (100 kD $\sim$ 300 kD) 络合元素最少; 对于 REEs、Cu 等, 其在各分子量段 DOM 上的分布呈现较均匀的趋势。

**关键词:** 聚合物络合超滤; 电感耦合等离子体质谱; 凝胶色谱; 海水; 痕量元素

## Abstract

Distribution characteristics and concentration of trace elements in seawater play a crucial role for investigation of marine ecosystem and global biogeochemistry. Because their low concentration and complicated matrix, analysis of trace element in seawater is a challenging field. Hence, the procedure of matrices separation, such as co-precipitation, solvent extraction, and chelating-resin adsorption was applied for analysis of trace level of elements in seawater in former studies, as well as there still have their respective limitations in complicated manipulation, high reagent consumption, and relatively high method blank. So developing some analytical methods with low method blank, and low limit of detection, good precision and accuracy is very important.

Polymer complexation-ultrafiltration (PC-UF) technique and inductively coupled plasma mass spectrometry (ICP-MS) detection were combined for the speciation and determination of trace elements in coastal and estuarine seawater. Afterwards, a methods for studying the molecular size distribution characteristics of dissolved organic matter-metal (DOM-M) complexes by UF-ICP-MS were developed and applied in coastal and estuarine seawater, which provided technical support and theoretical basis for the research on biogeochemistry of trace elements in seawater. At last, gel permeation chromatography (GPC) and ICP-MS was studied to give a rapid and accurate procedure for the measurement of complexation stability constant and average coordination number of polyethylenimine groups participating in the complex formation of polyethylenimine (PEI) with metal ions was proposed. The main contents and results are as follows:

(1) A method using PC-UF for matrix separation and determination by ICP-MS of trace elements in coastal and estuarine seawater has been developed. Metal ions and PEI were combined together when pH was above 7.5, and the salinity of seawater had no effect on the forming and the stability of the polymer-metal complex. The addition of PEI in seawater at higher than 20 mg/L yielded to prominent recoveries for all metal ions. The time for PEI binding with metal ions need to be longer than 25 min at room temperature to obtain better separation and recoveries, which suggest that the binding time could be reduced when higher temperature is available. The PEI-metal complex could be absolutely dissociated and eluted from the ultrafilter by 2.5 mL of 3% (v/v) nitric acid. Full quantitative data collection mode and internal

standard calibration curve were used for ICP-MS measurement. Under the optimized conditions, the relative standard deviations (RSDs) were lower than 9.3% (0.20  $\mu\text{g/L}$ ,  $n=5$ ), and the standard added recoveries were 78.7% (Ag) ~95.2% (Cu). Limits of detection (LODs,  $10\sigma$ ) were from 1.2 (Cd) to 9.8 (Cu) ng/L. The developed method has been applied to simultaneously determinate the metals in coastal and estuarine seawater.

(2) A method using PC-UF for matrix separation and determination of 24 elements at trace level in coastal and estuarine seawater by ICP-MS has been developed. Full quantitative data collection mode and internal standard calibration curve were used for ICP-MS measurement. Under the optimized conditions, the RSDs were in the range of 1.74% (Cd) and 7.34% (Eu) (0.02  $\mu\text{g/L}$ ~0.10  $\mu\text{g/L}$ ,  $n=3$ ), and the standard added recoveries were 72.8% (Ag) ~95.8% (Sm). LODs ( $10\sigma$ ) were from 0.23 ng/L (Ho) to 13.9 ng/L (Pb). The developed method has been applied to simultaneously determinate the Rare Earth Elements (REEs) and metals in coastal and estuarine seawater.

(3) A rapid and accurate procedure using gel permeation chromatography (GPC) technique and ICP-MS for the measurement of complexation stability constant and average coordination number of polyethylenimine (PEI) groups participating in the complex formation of PEI with metal ions has been proposed. The method was applied for the determination of the stability constant and average coordination number of PEI and  $M^{z+}$  complex. Firstly, various initial concentration ratios of PEI and  $M^{z+}$  solution were prepared separately, and then mixed until the complexation equilibrium were reached, at last, different  $M^{z+}$  and PEI-M were separated and determined by GPC-ICP-MS. With the help of chemical model inferred in the study, complexation stability constants and average coordinating numbers of PEI-M could be calculated. The effect of pH (4.1~5.3) on the equilibrium was investigated, which showed that the complexation stability constants and average coordinating numbers of PEI-M became larger as pH increased. This might due to the protonation of PEI reduced as pH increased, then the ability of PEI complex with metals became stronger.

(4) A method for studying on molecular size distribution characteristics of DOM-M complexes in coastal and estuarine seawater by UF-ICP-MS was developed, which had low blank, high sensitivity, good reproducibility, multi-sample handling,



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