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厦门大学

硕士学位论文

近岸海水中痕量重金属的膜富集及快速检测方法的研究及现场应用

Study of Membrane Pre-concentration Coupled with Fast Detection and on-site Application to the Analysis of Trace Heavy Metals in Coastal Seawater

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摘 要

众多重金属元素中，有些是海洋浮游植物生长所必需的微量营养元素，有些则是非生命所需，即使浓度很低也对生命体具有毒害作用。大洋海水中重金属浓度极低，通常在 ng L^{-1} 水平。河口及近岸海域由于人为输入的影响，重金属含量较高。了解近岸海域海水中重金属的含量、分布及其形态等，有助于更好地了解重金属的污染来源、环境行为及可能产生的生态毒理效应。目前海水中重金属的分析，一般是将样品采集后带回实验室，进行预处理后再以原子光谱或质谱法测定。由于样品在运输、保存过程中可能引入污染，且重金属形态易发生变化等原因，将导致测定值有较大偏差。因此，现场测定成为海水中重金属分析的发展趋势。

本论文针对现有方法的不足，研究了滤膜富集技术对近岸海水中痕量重金属的分离富集，以及可用于现场的分光光度及手持式 X 射线荧光等快速检测技术。主要内容及结果如下：

（1）建立了水体中痕量铁的 Fe(II)-菲咯嗪-CTAB 离子对化合物形成-膜富集-乙醇+硝酸洗脱-分光光度测定法。Fe^{2+}与菲咯嗪反应生成的阴离子络合物 Fe(II)-菲咯嗪，可与阳离子表面活性剂十六烷基三甲基溴化铵（Cetyltrimethylammonium bromide, CTAB）反应，生成的大分子离子对化合物 Fe(II)-菲咯嗪-CTAB 可被微孔滤膜截留富集，并由乙醇+硝酸溶液洗脱，进而由分光光度法检测。在优化的实验条件下，本方法具有良好的重现性和灵敏度，于不同时间测定含铁 10 μg L^{-1} 的水样 9 次，RSD 值为 3.9%；选取不同的试样富集体积，可将定量分析线性范围扩展为 0.5-120 μg L^{-1}；方法检测限为 0.19 μg L^{-1}；实际海水基底加标的回收率在 97.2-109%之间。用本方法在现场对 12 个海水样进行了测定，并将其中两个水样带回至实验室用 ICP-MS 法测定，*t* 检验结果表明，两种方法无显著性差异。本方法还应用于现场测定“铁加富实验”海水中可溶态铁浓度。本方法操作简便、测定成本低，适用于海洋现场分析。

（2）在上述实验基础上，建立了水体中痕量铁的膜富集-固相分光光度测定法。方法线性范围 2.5-120 μg L^{-1}，检测限为 1.65 μg L^{-1}。对实际淡水及海水水样

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进行了测定，基底加标回收率在113-127%之间。平行测定含铁浓度10 μg Ł$^{-1}$的超纯水加标试样9次， RSD值为5.8%。本法对实际海水的测定结果与膜富集-乙醇+硝酸洗脱-分光光度测定法无显著差异。以固相分光测定法代替了用乙醇+硝酸洗脱的溶液分光测定法，省却洗脱步骤，取膜直接测定，节约试剂并减化了操作步骤，对样品的快速测定具有重要意义。

（3）建立了近岸海水中多种重金属（铁、镍、锰、铜、锌及铅）的氢氧化物沉淀/共沉淀-膜富集-XRF 测定法。在海水样品中加入氢氧化钠溶液，使海水中大量的Mg^{2+}生成氢氧化镁沉淀，其他金属离子如Fe^{2+}、Fe^{3+}、Ni^{2+}、Mn^{2+}、Cu^{2+}、Zn^{2+}及Pb^{2+}等或生成氢氧化物，以沉淀或与氢氧化镁共沉淀的形式经过滤截留富集在膜上，膜上的目标物直接由手持式 X 射线荧光仪检测。在优化的实验条件下，以重金属含量极低的台湾海峡表层过滤海水作为工作曲线溶液的基底，方法的线性范围为12.5-400 μg Ł$^{-1}$，检测限在1.32-7.84 μg Ł$^{-1}$之间。对各重金属浓度为 100 μg Ł$^{-1}$的海水基底加标试样连续测定 7 次，各金属元素的 RSD 值在3.73-4.86%之间。用本方法成功测定了厦门近岸海域水样中可溶态重金属的浓度。本方法对海水中可溶态铁的分析与用方法（1）获得的结果无显著差异。

（4）建立了近岸海水中痕量重金属（铁、镍、锰、铜、锌及铅）的硫化物沉淀/共沉淀-膜富集-XRF 测定法。选用硫化钠溶液作为沉淀剂，在海水样品在加入硫化钠溶液后，待测金属元素同时发生沉淀及共沉淀反应，经过滤可截留富集在膜上，由手持式 X 射线荧光仪直接测定。在优化的实验条件下，以重金属含量极低的台湾海峡表层过滤海水作为工作曲线溶液的基底，方法的线性范围为12.5-400 μg Ł$^{-1}$，检测限在1.94-11.0 μg Ł$^{-1}$之间。对各金属浓度为100 μg Ł$^{-1}$的海水基底加标试样连续测定7次，各金属元素的RSD值在4.43-6.43%之间。用本方法成功测定了厦门西港及九龙江河口海水中重金属浓度。本方法对实际海水的测定结果与ICP-MS法测定结果无显著差异。

基于样品酸化与否及过滤先后顺序的不同，本论文所建立的各种分析方法，均适合用于水样中可溶态、溶解态及游离态重金属的分析。

关键词：膜富集；近岸海水；痕量铁；重金属；共沉淀

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ABSTRACT

Some heavy metals are essential trace elements for phytoplankton in marine environment, while some are not and can cause toxic effects even at low concentrations. In open-ocean waters, concentrations of heavy metal are down to ng L^{-1} levels. In estuary and coastal area, the concentrations can be higher because of human activities. Study on the concentrations, distributions and species of heavy metals can help to better understand their pollution sources, environment behaviors and ecological toxicological effects. To analyze heavy metals in seawater, the collected samples are ordinarily shipped back to laboratory for determination. Since samples can be contaminated during transportation and preservation, and the speciation of the heavy metals can be changed, thus deviation may be induced to the analytical results. To overcome these problems, on-site analysis has become the trend of technique development.

In order to make up deficiencies of the existing methods, this thesis focused on the technique of membrane filtration, on-site spectrophotometric and XRF detection, and its application to the fast analysis of heavy metals in coastal seawater samples. The main contents and results are as follows:

(1) A membrane pre-concentration method coupled with ethanol-nitric acid elution and spectrophotometric detection has been established for the determination of trace amount of iron in natural water. It was found that Fe(II)-ferrozine complex could react with cetyltrimethylammonium bromide (CTAB) to form Fe(II)-ferrozine-CTAB ion-pair compound, which could be collected on membrane by filtration with suction. The Fe(II)-ferrozine-CTAB ion-pair compound collected on membrane could be eluted with ethanol-nitric acid mix solution and detected with a spectrophotometer. Under the optimized conditions, the RSD (n=9) was 3.9% for a sample containing 10 μg L^{-1} of iron and measured at different time. The calibration curves showed a linear range between 0.5 and 120 μg L^{-1}, and the detection limit and recoveries of the

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proposed method were found to be 0.19 μg·L^{-1}and 97.2-109%. Twelve seawater samples were analyzed on-site with the proposed method and two were additionally with ICP-MS method. No significant difference was shown between the two methods with *t*-test. The method has also been used in an on-site "iron enrichment experiment" with phytoplankton to determine dissolvable iron, and approved to be simple, inexpensive and practicable.

(2) Based on the above work, a membrane pre-concentration method coupled with solid-phase spectrophotometric detection has been established for the determination of trace amount of iron in natural water. The calibration curves showed a linear range between 2.5 and 120 μg·L^{-1}, and the detection limit and recoveries of the proposed method were found to be 1.65 μg·L^{-1}and 113-127%. The RSD (n=9) was 5.9% for a sample containing 10 μg·L^{-1} of iron and measured repeatedly. Iron in the seawater samples were analyzed with both the proposed method and the method (1), and the results showed no significant difference with *t*-test. The proposed method could analyze the membrane directly and need fewer reagents and operations, which is important to fast analysis.

(3) A membrane pre-concentration method coupled with hydroxide precipitation/ co-precipitation and XRF detection has been established for the determination of heavy metals (Fe, Ni, Mn, Cu, Zn, Pb) in coastal seawater. The Mg^{2+} in seawater could form precipitate as $Mg(OH)_2$ when NaOH solution was added, and the heavy metal ions could form hydroxide precipitates or deposit with $Mg(OH)_2$. Then the precipitates containing target metals could be filtrated on membrane and detected with a portable XRF. Under the optimized conditions, using Taiwan Strait surface seawater as a matrix, the linear range was found to be 12.5 to 400 μg·L^{-1}, the detection limits for the metals were between 1.32 and 7.84 μg·L^{-1}. The RSD (*n*=7) was 3.73-4.86% for a sample containing 100 μg·L^{-1} of each metal and measured repeatedly. The proposed method was successfully applied in the laboratory to determine seawater samples obtained from Xiamen coastal sea area. The samples were also analyzed with method (1), and the results for dissolvable iron showed no significant difference with

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t-test.

(4) A membrane pre-concentration method coupled with sulfide precipitation/ co-precipitation and XRF detection has been established for the determination of heavy metals (Fe, Ni, Mn, Cu, Zn, Pb) in coastal seawater. When sodium sulfide solution was added to seawater, the target metals formed precipitate and could be filtrated on membrane and detected with a portable XRF. Under the optimized conditions, using Taiwan Strait surface seawater as a matrix, the linear range was found to be 12.5 to 400 μg L^{-1}, the detection limits for the metals were between 1.94 and 11.0 μg L^{-1}. The RSD (n=7) was 4.43-6.43% for a sample containing 100 μg L^{-1} of each metal and measured repeatedly. The proposed method was successfully applied in the laboratory to determine seawater samples obtained from Xiamen western harbour and Jiulongjiang Estuary. Two seawater samples were analyzed with the proposed method and ICP-MS method. No significant difference was found between the two methods with *t*-test.

Based on whether the samples are acidified and filtered before or after acidification, the methods established in this thesis are applicable to the analysis of dissolvable, dissolved and free heavy metals in water samples.

Keywords: membrane pre-concentration; coastal seawater; trace iron; heavy metals; co-precipitation

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