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厦门大学

硕士学位论文

海水溶解无机碳原位测定仪的研制

Development of *In Situ* Analyzer for Seawater Dissolved
Inorganic Carbon

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摘要

海水溶解无机碳(Dissolved Inorganic Carbon, DIC)是表征海水碳酸盐体系的四大参数之一,也是海洋碳循环和海洋酸化研究的基础数据。目前,海水 DIC 数据的获取主要依靠科考船采集离散的样品进行分析,由此得到的数据时空分辨率低,无法满足当前海洋科学研究的需求。采用原位仪器进行长时间系列观测是获取高时间分辨率海水 DIC 数据的最佳手段。目前仍鲜有 DIC 原位测定仪的报道。本论文研制了原位 DIC 测定仪(*In Situ Analyzer of Dissolved Inorganic Carbon, ISA-DIC*),并在实验室、室外水池和海上对其进行性能测试。主要研究内容和结果如下:

- (1) 以分光光度法测定 pH 的原理为基础,采用八通阀切换流路的方式酸化海水,并以透气性能良好的 Teflon AF2400 管制作二氧化碳平衡器,利用自制的以 LED(Light Emitting Diode, LED)为光源的分光系统测定 Teflon AF2400 管内指示剂溶液的 pH,研制了 ISA-DIC。所研制测定仪的重量为 6.5 kg,功耗约 4.1W。仪器测定单个样品消耗指示剂溶液约 80 μL 、盐酸 100 μL ,耗时 6 min。露天水池中 10 天的测试结果表明测定仪的精密度为 $\pm 4.2 \mu\text{mol/kg}$,其测定结果与红外吸收法(标准方法)的测定结果之间的符合程度即准确度为 $1.7 \pm 7.8 \mu\text{mol/kg}$,未观察到显著的信号漂移。在三亚海域的原位海试实验中,ISA-DIC 完全正常工作,获得了 31 天的原位观测数据,但准确度仅为 $23.7 \pm 27.7 \mu\text{mol/kg}$ 。
- (2) 针对仪器存在的不足,对 ISA-DIC 的八通阀控制器及海水泵进行改进,并测试其性能。结果表明,ISA-DIC 在实验室的精密度为 $\pm 2.5 \mu\text{mol/kg}$ 。在 7 天的三亚海试中,ISA-DIC 完全正常工作,准确度为 $8.9 \pm 15.5 \mu\text{mol/kg}$ 。这些结果说明,改进后的 ISA-DIC 的性能得到明显的改善,尤其是准确度和可靠性。总之,本论文成功研制了可用于实际海洋环境中海水 DIC 的长时间系列观测的原位 DIC 分析仪,其具有重量轻、功耗低和精密度高的特点,但准确度还需进一步提高。

关键词：海水；溶解无机碳；分光光度法测 pH；原位测定仪

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ABSTRACT

Dissolved inorganic carbon (DIC) is one of the four parameters characterizing the oceanic CO₂ system, and also the basic data for the research of ocean carbon cycle and ocean acidification. So far, most of the DIC data is obtained mainly by analyzing bottle samples collected in cruise. This data is of low spatial and temporal resolution and can not meet the requirement of the research community. Time series observation using *in situ* analyzers is the best way to obtain DIC data of high temporal resolution, however very few *in situ* DIC analyzers have been reported. In this study, we developed an *in situ* analyzer for seawater DIC (ISA-DIC) and tested its performance in laboratory, outdoor tank and at sea. The obtained results are shown as follows:

- (1) The ISA-DIC is based on spectrophotometric pH measurement. An 8-port 2-position valve was used to allow seawater sample and hydrochloric acid mix at a constant volume ratio. The Teflon AF2400 tubing which has very high gas-permeability was used to make a CO₂-equilibrator. A home-made spectrophotoelectric system using LEDs as the light source was applied to measure the pH of the indicator inside the Teflon AF 2400 tubing. The weight and power consumption of ISA-DIC were 6.5 kg and 4.1 W, respectively. 80 μL of indicator, 100 μL of hydrochloric acid and 6 min were needed for one measurement. The 10-day test in outdoor tank showed that the precision of ISA-DIC was 4.2 μmol/kg; the agreement between the measurements obtained by ISA-DIC and gas-phase NDIR (standard method), the accuracy, was 1.7±7.8 μmol/kg, and no obvious drift was observed during the test. During the test in Sanya bay, ISA-DIC ran smoothly and the long-term time series DIC data of 31 days was obtained. However, the accuracy at sea of the ISA-DIC should be improved.
- (2) The ISA-DIC was modified by using home-made valve controller and peristaltic pump to improve its performance. After modification, the test in lab indicated that

the precision was $\pm 2.5 \mu\text{mol/kg}$. During the 7-day test at Sanya bay, ISA-DIC ran smoothly and showed an accuracy of $8.9 \pm 15.5 \mu\text{mol/kg}$. No obvious signal drift occurred. In brief, the ISA-DIC is small in size and with low power consumption, and it can be applied in the long-term time-series observation of DIC at sea. However, more work is needed to improve its accuracy.

Key words: seawater; dissolved inorganic carbon; spectrophotometric pH measurement; *in situ* analyzer

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缩略语表

BCP	Bromocresol Purple	溴甲酚紫
CRM	Certified Reference Material	标准参考物质
CTD	Conductance Temperature Depth	温盐深探测仪
DIC	Dissolved Inorganic Carbon	溶解无机碳
$p\text{CO}_2$	The partial Pressure of CO_2	二氧化碳分压
$f\text{CO}_2$	The Fugacity of CO_2	二氧化碳逸度
TA	Total Alkalinity	总碱度
FEP	Fluorinated Ethylene Propylene	氟化乙烯丙烯共聚物
HDPE	High Density Polyethylene	高密度聚乙烯
PEEK	Polyetheretherketone	聚醚醚酮
PMMA	Polymethylmethacrylate	聚甲基丙烯酸甲酯
PTFE	Polytetrafluoroethene	聚四氟乙烯
PVC	Polyvinylchloride	聚氯乙烯
POF	Plastic Optical Fiber	塑料光纤
ISA-DIC	<i>In Situ</i> Analyzer of Dissolved Inorganic Carbon	溶解无机碳原位测定仪
LED	Light Emitting Diode	发光二极管
CCD	Charge-Coupled Device	电荷耦合检测器
NDIR	Non-Dispersive Infra-red	非色散红外

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