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硝酸盐传感器在深海压力下的校准方法

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摘　要：研究表明,海水中溴化物的紫外吸收光谱受到深海压力的影响会影响海水中硝酸盐的测量准确度。现有的水下硝酸盐传感器已暴露出测量误差大,环境适应性差、无法应用于 2 000 m 以下的深海探测等问题。因此,为了更准确地计算硝酸盐浓度,有必要开展深海压力对海水紫外吸收光谱的校正研究。实验室对模拟深海压力环境中的硝酸盐进行测试试验,提出了两种算法用来矫正压力下的紫外光谱,通过实验验证了这两种压力校正算法对硝酸盐计算的预测准确性。结果表明,多元散射校正-偏最小二乘法回归校正算法具有最好的测量效果,R^2为 0.997,平均绝对误差 (MAE) 为 1.294 μmol/L,平均偏差误差 (MBE) 为 0.037 μmol/L。

关键词：硝酸盐；　压力校正；　紫外光谱法；　多元散射校正

中图分类号：O433.4　　**文献标志码：**A　　**DOI：**10.3788/IRLA20240095

硝酸盐作为天然水域中主要初级生产所需的氮源,其在 217~240 nm 紫外光谱区展现出的光学活性为光学检测提供了可能[1]。近年来,基于紫外分光光度法测量海水中的硝酸盐得到了广泛应用。相较于传统的化学法,该方法具有明显优势,包括免除化学试剂使用、避免了对生态系统造成二次污染,便于长期原位测量等。然而,光学硝酸盐测量在相关光谱范围内受到海水中基质 (如溴化物) 的影响[2],紫外光谱的强度会产生偏移。在压力下,海水的紫外吸收光谱与溴化物浓度之间也存在着压力系数。基于此,国外研究人员提出了 2000 m 内的压力校正方程,提高了测量准确度[3]。

对深海资源开发而言,实现对硝酸盐的原位准确测量对于构建海洋采矿环境的预警检测与评价体系至关重要。当前能够应用于深海的硝酸盐传感器产品在市面上非常少,且都依赖于进口,价格昂贵,因此,掌握深海硝酸盐传感器测量的关键技术,对建设透明海洋至关重要。以美国海鸟公司的 Deep SUNA 为例,其可以达到的水下深度约为 2000 m,而 2000 m 以下的海水硝酸盐检测技术还存在空白。因此,文中提出了一种面向 0~50 MPa 压力范围的硝酸盐测量的校正方法,旨在扩大硝酸盐传感器的应用深度,并且能提高深海下的测量准确度。

测量系统如图 1 所示。氘灯 (DH-2000-DUV, 海洋光学) 发出的光通过光纤分束器 (定制, 闻奕光电, Ltd) 后分为两路,一路通过光纤衰减器 (FVA-UV, 海洋光学),另一路通过压力容器,从而能够同步监测光源发光强度的稳定性及消除光源波动带来的测量误差。两路 UV 光在光开关处汇聚,并通过光开关选择传输路径,最后由数据处理模块进行数据采集和计算。小型压力罐上方接活塞压力计,由活塞压力计在 0~50 MPa 的范围给海水加压模拟海水的受压情况,并通过紫外光谱仪 QE-Pro 测量不同压力下的紫外吸收光谱数据。同时利用连续流动分析仪 (AutoAnalyzer 3, SEAL) 测量鳌山湾海水基底中的硝酸盐浓度,而后在鳌山湾海水中加入不同量的硝酸盐含量 (0~50 μmol/L),以制备成不同硝酸盐浓度的海水样品,明确每个样品的浓度,比对系统的测量误差。

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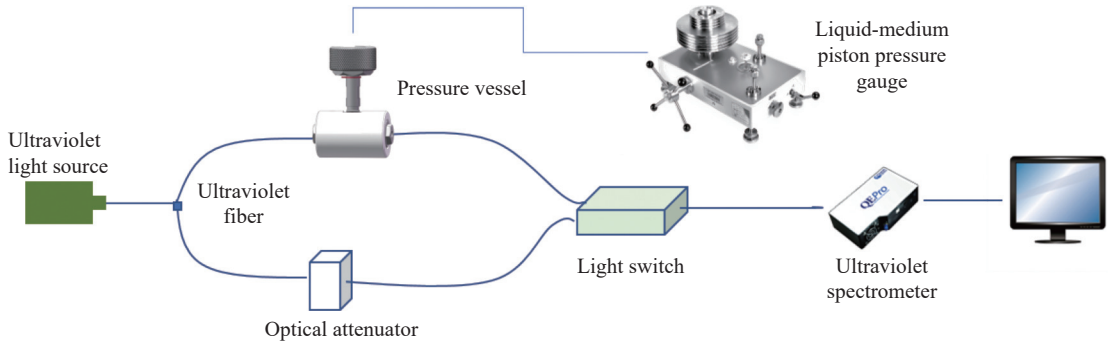
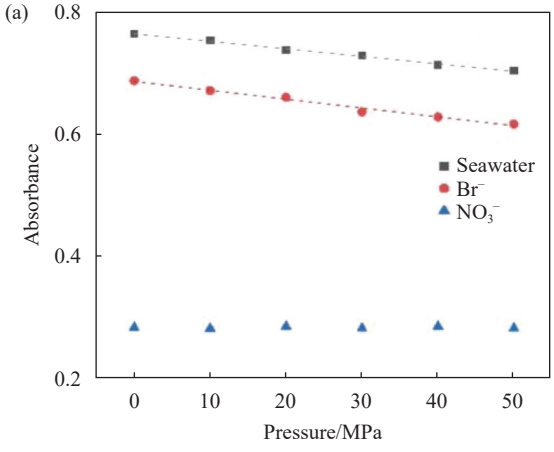


图 1 压力对海水紫外吸收光谱影响的测量系统

Fig.1 System for measuring ultraviolet spectra of seawater under pressure

测量结果表明，随着压力的增加，海水样品在200~220 nm 范围的吸光度减小。为了研究海水中不同基质受压力影响产生的变化，分别对硝酸盐溶液(50 μmol/L)、鳌山湾海水和溴化钠溶液 (840 μmol/L)做了相同的压力测试，得到的吸光度结果如图 2(a) 所示。可以看出在压力下海水的吸光度和溴化物吸光度的趋势一致，而硝酸盐的吸光度基本不受压力的影响。因此，利用两种光谱预处理算法 (包括变量标准化变换 (SNV) 和多元散射校正 (MSC)) 对 0~50 MPa 范围海水紫外吸收光谱进行了压力校正，并用偏最小二乘回归 (PLS) 算法进行回归预测研究，结果如图 2(b) 所示。可以看出，未使用压力校正算法的 R^2 为 0.991，平均绝对误差 (MAE) 为 1.980 μmol/L，平均偏差误差 (MBE) 为 −0.042 μmol/L，均方根误差 (RMSE) 为 2.505 μmol/L。使用 MSC-PLS 算法的 R^2 为 0.997，MAE 为 1.294 μmol/L，MBE 为 0.037 μmol/L，RMSE 为 1.620 μmol/L。使用 SNV-PLS 算法的 R^2 为 0.989，MAE 为 2.308 μmol/L，MBE 为 0.098 μmol/L，RMSE 为 3.085 μmol/L。因此，使用 MSC-PLS 压力校正算法有最大的 R^2 和最小的均方根误差，比未使用压力校正算法的效果更好，具有最好的压力校正和数据预测效果。



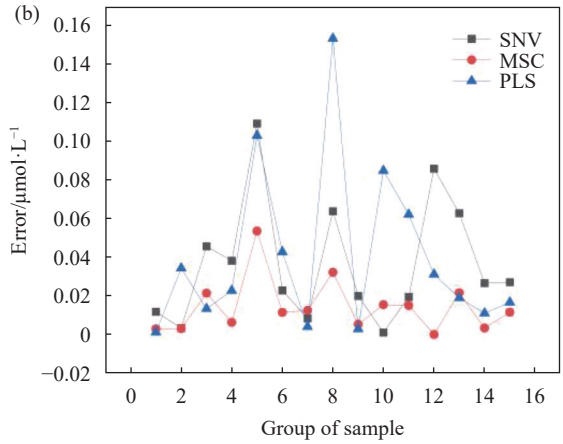


图 2 (a) 不同溶液在 214 nm 光波长处吸光度与压力的关系；(b) 不同算法的预测误差

Fig.2 (a) Absorbance of different solutions under pressure at 214 nm; (b) Prediction error of different algorithms

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Correction of pressure effect in calibrating nitrate concentration of seawater

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Abstract:

Objective Optical nitrate sensors have advantages for in-situ exploration and the potential for long-term observation in deep-sea environment. However, measurement of optical nitrate is influenced by substrates in seawater, especially bromide ions (Br^-), within the relevant spectral range, causing a spectral shift in the ultraviolet (UV) intensity spectrum. In recent years, the pressure coefficient of the UV absorption spectrum of bromine under seawater pressure of 2 000 meters has been studied and experimentally confirmed, that the bromide in seawater affects the UV absorption spectrum. Considering that the seabed minerals are primarily distributed undersea at depths ranging from 1 000 to 6 000 meters, achieving accurate in-situ detection of nitrate concentration becomes crucial for the assessment of impact of seabed mining on the marine eco-system, establishment of an early warning system for the marine mining environment. Currently, products of nitrate sensors are limited to the submerged depths of approximately 2 000 meters. No nitrate sensor product is available beyond this depth. This paper reports a calibration method for nitrate measurements within the pressure range of 0-50 MPa (0-5 000 meters), aiming to improve the accuracy of nitrate measurements in deep-sea environments.

Methods A system capable of measuring the UV spectrum of seawater under deep-sea pressure is constructed in this work. The light emitted from a deuterium lamp is transmitted through a fiber-optic beam splitter, dividing it into two paths. One path passes through a fiber-optic attenuator, while the other path goes through a pressure vessel. The two signals are then combined at an optical switch and selectively transmitted through it. Finally, the data processing module performs data acquisition and calculation. To simulate the deep-sea environment, the pressure vessel is connected to a weight manometer. The UV absorption spectra at different pressure are measured by controlling the external pressure. A continuous flow analyser was used to calibrate the nitrate concentration in the seawater samples collected from Aoshan Bay. Different levels of nitrate (0-50 μmol/L) were added to the Aoshan Bay seawater, and these seawater samples with different nitrate concentrations were measured by the measurement system.

Results and Discussions The measurement results revealed a decrease in the absorbance of seawater samples with an increase in pressure. To investigate the pressure-induced changes in different substrates in seawater, identical pressure tests were conducted for nitrate solution (50 μmol/L), Aoshan Bay seawater, and sodium bromide solution (840 μmol/L). The absorbance results obtained are depicted in Fig.2(a). Notably, the absorbance of seawater and bromide under pressure exhibited a similar trend, whereas the absorbance of nitrate remained largely unaffected by pressure. Subsequently, pressure correction of seawater UV absorption spectra was

conducted at pressures ranging from 0 to 50 MPa using two algorithms for spectral pre-processing, including standard normal variate transform (SNV) and multiplicative scatter correction (MSC), and regression prediction with the partial least squares regression (PLS) algorithm. The results are presented in Fig. 2(b). It is evident that the R^2 is 0.991, MAE is 1.980 μmol/L, MBE is −0.042 μmol/L, and root mean square error (RMSE) is 2.505 without using any pressure correction. The R^2 is 0.997, MAE is 1.294 μmol/L, MBE is 0.037 μmol/L, and RMSE is 1.620 using the MSC-PLS algorithm. The R^2 is 0.989, MAE is 2.308 μmol/L, MBE is 0.098 μmol/L, and RMSE is 3.085 μmol/L using the SNV-PLS algorithm. Therefore, with the utilization of the MSC-PLS pressure correction algorithm, the prediction results are superior to those without using any pressure correction. This suggests that the pressure correction algorithm improves measurement accuracy. The MSC-PLS algorithm has the highest R^2 and the smallest error range, indicating its superior pressure correction and data prediction capabilities.

Conclusions The primary objective of this study is to enhance the accuracy of optical nitrate measurements in the deep-sea environment by addressing the influence of substrates such as bromide on UV absorption spectra. A system capable of measuring the UV spectrum of seawater under deep-sea pressure is constructed, utilizing a deuterium lamp, fiber-optic components, and a pressure vessel. The experimental results demonstrate variations in UV absorption spectra between 200-240 nm under different pressure conditions at the same nitrate concentration. The SNV and MSC algorithms are employed for pressure correction, and MSC-PLS algorithm exhibits superiority in predicting nitrate concentrations under the pressure range of 0-100 MPa (R^2 of 0.997). Therefore, the proposed method offers potential applications in mining exploration and environmental monitoring.

Key words: nitrate measurement; pressure correction; ultraviolet spectroscopic measurement system; multiplicative scatter correction

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