A method for calibrating seawater polyaromatic hydrocarbons sensor

Li Zhang*, Yang Wang, Xiangfeng Kong, Jingru Wang, Zhaoyu Wang
Institute of oceanographic Instrumentation, Qilu University of Technology (Shandong Academy of Sciences) Qingdao 266061, China
*Corresponding Author (only one email address here): zhangggg@qlu.edu.cn

Abstract. To solve the problems in the calibration of polyaromatic hydrocarbons sensor used in seawater, we proposed a new method that using 1,5-Naphthalenedisulfonic acid, disodium salt dihydrate instead of polyaromatic hydrocarbons standard substances to calibrate seawater polyaromatic hydrocarbons sensor. Relative to polyaromatic hydrocarbons standard substances, 1,5-Naphthalenedisulfonic acid, disodium salt dihydrate shows higher solubility in seawater, better stability under the detection wavelength of polyaromatic hydrocarbons and lower toxicity to organisms. Our results showed that the relative errors between real concentrations of standard substances and measuring concentrations of these standard substances via 1,5-Naphthalenedisulfonic acid, disodium salt dihydrate-calibrated sensor varied from 5~15%. Our method can reduce the complexity of calibration procedures, and keep the accuracy and precision of sensors in the determination of polyaromatic hydrocarbons in seawater.

1. Introduction
With the intensification of anthropogenic activities in recent years, environmental pollution is becoming more and more serious. The occurring frequency of pollution events in marine environment increased at a stunning speed. Amongst, oil pollution was one of the most highlighting events[1]. Enormous events of oil spill, such as oil spill in the Gulf of Mexico and Bohai bay, and of oil leakage in offshore platforms of oil production, caused strong impacts on marine ecosystem and heavy losses of local economy [2]. It is urgent to improve the monitoring capability of crude oil pollutants, especially the capability of in-situ, real-time, and continuously monitoring and analysis of petroleum pollutants[3-4].

The determination of marine crude oil in lab was often conducted by the methods of UV spectrophotometry, infrared spectrophotometry, fluorescence spectrophotometry, weight method, gas phase - mass spectrometry [5]. The results of these lab-methods are accurate. However, during the transportation from sampling sites to lab, oil samples are vulnerable to the fluctuation of light and temperature and must be stored carefully. In the process of analysis, furthermore, sample pretreatment is time-consuming, and organic solvents used in these methods may cause damages to the health of technicians and cause secondary pollution to the environment. Compared to these lab methods, the in-situ monitoring by sensor can be conducted in situ without the addition of organic chemicals, it thus avoids sample transportation and damages to technicians and environment. It also shows high sensitivity to crude oil, and has become a widely used method for the determination of crude oil in water [6].

Substances with fluorescence in crude oil is the monitoring target of sensors. The fluorescence of crude oil result from aromatic hydrocarbons, which are one of the most important components of crude oil and source rocks, generally accounting for 10% ~ 45% of the total hydrocarbons and including hundreds of compounds. Aromatic hydrocarbons refer to the compounds containing unsaturated benzene
rings, which can be divided into single rings, polyrings (independent benzene rings) and thick rings (benzene rings share adjacent carbon atoms). When aromatic compounds are affected by environmental factors, such as mixing of aromatic compounds of different types, substituents, halogen elements, metal cations, solvents, temperature and hydrogen bonds, the peak position and intensity of fluorescence will change \(^7\). Oil can be separated into four components: saturated hydrocarbon, aromatic hydrocarbon, non-hydrocarbon and asphaltene. Because saturated hydrocarbons do not fluoresce and asphaltene fluorescence is very weak, aromatics and non-hydrocarbons are the leading source of fluorescence in crude oil.

The calibrating process in seawater for oil in-situ sensors is complex and inaccurate due to the complexity of crude oil components and the variation of fluorescence even at the same concentration of crude oil. Therefore, a method that can reduce the complexity and inaccuracy of the calibration of oil in-situ sensor is urgently needed. In this paper, a new method is proposed to realize the rapid calibration of polyaromatic hydrocarbons sensor in seawater. It can help the fluorescence signals collected by sensors transform to the concentration of crude oil at a well-proportional scale, keep the accuracy of oil in-situ sensor, and reduce the complexity of calibrating process.

2. Methods

In the present study, we proposed a method for calibrating a petroleum sensor using water-soluble compounds instead of petroleum standard substances. The compounds used in our study are easily soluble in water and have good fluorescence efficiency under the detection wavelength. The specific operation is as follows:

2.1. Spectroscopic experiments on petroleum standard substances

A series of concentration gradients of standard petroleum substances (HJ Oil Standard) were prepared. The fluorescence values were detected under the excitation wavelength of 254 nm and emission wavelength of 360 nm according to the method of GB 17378.4-2007. The spectrogram of the oil standard substance was obtained by the scan of full emission spectrum (300-900 nm) at the excitation wavelength of 254 nm (Figure 1a). The standard curve of petroleum concentrations vs. fluorescence values at 360 nm was shown in Figure 2.

2.2. 1,5-Naphthalenedisulfonic acid disodium salt spectrum experiment

A series of concentration gradients of 1,5-Naphthalenedisulfonic acid, disodium salt dihydrate were prepared. Fluorescence detection was performed under the excitation wavelength of 254 nm and emission wavelength of 360 nm, the full spectrum (300-900 nm) of 1,5-Naphthalenedisulfonic acid, disodium salt dihydrate was obtained at the excitation wavelength of 254 nm (Figure 1b). The standard curve of the concentrations of 1,5-Naphthalenedisulfonic acid, disodium salt dihydrate vs. fluorescence values at 360 nm was shown in Figure 3.

2.3. Sensor verification experiment

A series of concentration gradients of standard petroleum substances were prepared, and the sensor calibrated by 1,5-Naphthalenedisulfonic acid, disodium salt dihydrate was used to measure the concentration of standard petroleum substances. The relative errors between real concentrations and measuring concentrations of standard petroleum substances was calculated.

3. Results

1,5-Naphthalenedisulfonic acid, disodium salt dihydrate has fluorescence value at the wavelength of 360 nm, which can be used to calibrate the seawater polyaromatic hydrocarbons sensor instead of the petroleum standard substance (Figure 1). At the measuring wavelength, both petroleum standard substances and 1,5-Naphthalenedisulfonic acid, disodium salt dihydrate showed significant concentration-dependent relationships with fluorescence, and the linear-regression coefficients of greater than 0.99 were found (Figure 2 a and b).
The relative errors between the real concentrations of petroleum standard substances and the measuring concentrations of these standard substances by 1,5-Naphthalenedisulfonic acid, disodium salt dihydrate-calibrated sensor varied from 5 to 15% (Table 1).

| Petroleum standard substance concentration (mg/L) | Sensor test concentration (mg/L) | relative error (%) |
|--------------------------------------------------|----------------------------------|-------------------|
| 0.10                                             | 0.09                             | -10               |
| 0.20                                             | 0.17                             | -15               |
| 0.40                                             | 0.36                             | -12.5             |
| 0.80                                             | 0.75                             | -6.25             |
| 1.60                                             | 1.52                             | -5                |
| 3.20                                             | 3.08                             | -3.75             |

4. Discussion

We used 1, 5-naphthalenedisulfonic acid, disodium salt hydrate as a substitute of standard petroleum substance in the calibration of seawater polyaromatic hydrocarbons sensor. Compared with the standard petroleum substance, the reagent 1, 5-naphthalenedisulfonic acid, disodium salt hydrate is much easier to dissolve in seawater, thus can reduce the measuring errors which result from the stirring process when
preparing the aqueous solution of standard petroleum substances. Due to its great solubility to seawater, besides, the use of 1, 5-naphthalenedisulfonic acid, disodium salt hydrate may save time which was used to stir petroleum standard substances. Furthermore, the relatively low errors in our study also guarantee the accuracy of measurement when the sensor is calibrated by 1, 5-naphthalenedisulfonic acid, disodium salt hydrate.

5. Conclusions
Our study found the availability of 1, 5-naphthalenedisulfonic acid, disodium salt hydrate when calibrating polyaromatic hydrocarbons sensor in seawater, and suggested that 1, 5-naphthalenedisulfonic acid, disodium salt hydrate can be used as a substitute of standard petroleum substance in sensor calibration due to its solubility in seawater and low relative errors of measurement (<15%).

Acknowledgements
Authors acknowledge the financial support from the Natural Science Foundation of Shandong Province, ZR2019BD044; Research on Key Technologies of in situ oil pollutant sensor in seawater; National Key R&D Program of China, 2017YFC1404802; International Cooperation Project of Shandong Academy of Sciences, Development of marine ecological monitoring and early warning system, 2019GHPY15; Shandong Provincial Natural Science Foundation, China. ZR2019BD037. The Joint Funds of the National Natural Science Foundation of China (Grant No. U1806202); Scientific research project of Qilu University of Technology (Shandong Academy of Sciences), China. 2020QN0026.

References
[1] Srivastava P.; Sreekrishnan T.R.; Nema. A.K, 2018. Polyaromatic hydrocarbons: review of a global environmental issue, J. Hazard. Toxic Radioact. Waste. Vol.22(No.3):04018004.
[2] Naveen Kumar Arora, 2018. Bioremediation: a green approach for restoration of polluted ecosystems. Environmental Sustainability. Vol.1(No.4): 305-307
[3] Hodsona P.V.; Wallacelb S.J.; Sollah S.R.; Headd S.J. Heptichb; S.L.J.; Parrottc J.L.; Thomase P.J.; Berthiaumef A. Langloisb; V.S., 2020. Polycyclic aromatic compounds (PACs) in the Canadian environment: The challenges of ecological risk assessments. Environmental Pollution. Vol.266(Part 2): 115165.
[4] Trujillo-rodriguez M.J., Nacham O., Clark K.D., Anderson J.L., Ayala J.H., Afonso A.M., 2016. Magnetic ionic liquids as non-conventional extraction solvents for the determination of polycyclic aromatic hydrocarbons, Anal. Chim. Acta :106-113
[5] Santos, L.O.; Anjos dos J.P., Ferreira, S.L.C. and Andrade, J.B de, 2017. Simultaneous determination of PAHS, nitro-PAHS and quinones in surface and groundwater samples using SDME/GC-MS. Microchemical Journal Vol.133: 431-440.
[6] Xu Yanxin, Yang Yang, Zhao Minghui, Zhou Guangsen, Zhang Jing, Luo Xing, 2018. Research and Application for On-line Monitoring System of Oil Concentration in Water. Corrosion & Protection in petrochemical industry 35(1):20-22.
[7] Dai Jiacai, Guo Haimin, Song Hongwei, Xiao Zhuan, Cai Qiang, 2009. Preliminary Study of Oil Fluorescence Detection Methods and Its Application in Production Logging, Journal of Oil and Gas Technology,4(31):96-99
[8] Standardization Administration of China, General Administration of Quality Supervision, Inspection and Quarantine, PRC, 2007. The specification for marine monitoring—Part 4: Seawater analysis