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用于温度传感器原位在线校准的水三相点自动复现控制系统

乔志刚¹, 高德辛¹, 张牧子¹, 赵姗姗¹, 巫佳利¹, 苏娟¹, 陈胜功², 景超³,
刘海玲⁴, 杨博⁴, 吴琦^{1,2,3,4}

- (1. 山东大学海洋研究院, 山东青岛 266237;
2. 南方海洋科学与工程广东省实验室(广州), 广东广州 511458;
3. 青岛海洋传感器产业技术研究院, 山东青岛 266237;
4. 德州尧鼎光电科技有限公司, 山东德州 253084)

摘要: 温度传感器在长时间温度测量中会出现性能漂移导致测量误差, 为现场实时校准温度传感器实现长期稳定的高精度测量, 需要基于国际温标 ITS-90 规定的温度固定点, 对传感器进行无人自主原位校准。水三相点是水、冰、气三相平衡共存的温度点, 其温度为国际温标中的 0.01 °C 固定点, 是对传感器进行校准的最常用的固定温度点。水三相点瓶是再现水三相点的关键装置。相较于传统的玻璃外壳水三相点瓶, 金属外壳的水三相点瓶更为耐用, 更适用于自动原位校准。为了实现水三相点的自动复现, 根据高纯水自发相变原理, 设计了一种基于半导体帕尔贴效应快速稳定复现水三相点的自动控制及其控制方法。利用热电制冷器 (TEC) 和温度控制器为金属水三相点瓶提供过冷环境, 在基于模型的制冷调度算法控制下, 实现了较长时间保持稳定的水三相点状态。实验室测试表明, 该控制系统可以在 150 min 内达到 0.01 °C 的温坪, 并保持稳定的三相点温度 20 min 及温度波动度 ± 1 mK。温度原位在线自动校准系统可以为深海、深空及偏远地区的高精度温度测量提供校准服务。

关键词: 金属水三相点瓶; 温度原位自动校准装置; 温坪自动复现方法

中图分类号: O436 **文献标志码:** A **DOI:** 10.3788/IRLA20240096

水的三相点指的是水、冰和蒸汽三种物态同时存在的状态, 其平衡温度为 273.16 K(0.01°C)。在国际温标中, 水的三相点是定义热力学温度单位开尔文的唯一基准点, 也是 ITS-90 国际温标中最为重要的温度固定点之一^[1-2]。水的三相点的热力学温度复现对于实际温度测量具有至关重要的意义^[3]。

水的三相点复现是通过水三相点瓶内冻制冰套来实现。ITS-90 国际温标指南中广泛使用的是硼硅玻璃或熔融二氧化硅外壳的水三相点瓶。传统的复现方法包括冰盐混合物制冷法、干冰制冷法和液氮制冷法等, 这些方法都需要通过干冰、液氮或其他低温介质对水三相点瓶进行冷却, 在瓶内的高纯水结冰后, 再将其放入水槽中保存。这些传统方法的复现精度高, 效果良好, 但复杂度高, 操作难度大, 对操作

人员和环境要求较高, 不便于现场校准和集成应用^[2-3]。针对传统水三相点瓶和复现方法在现场原位应用中的局限性, 如深海中对温度传感器的原位校准, 文中基于自主研制的小型金属水三相点瓶, 研究了适用于温度传感器自动校准的小型化三相点复现控制系统。

该控制系统利用了金属水三相点容器中高纯水的自发相变原理, 结合基于半导体帕尔贴效应的热电制冷器 (TEC) 和温度控制电路, 实现了水三相点的自动复现和保持。通过使用热敏电阻和温度检测电路实现温度相变监测, 利用双热敏电阻和 TEC 构成闭环控制, 根据反馈电阻的温度差来调节 TEC 的驱动功率, 从而实现水三相点的自动复现和保持。

图 1(a) 和 (b) 分别为金属水三相点瓶自动复现系

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作者简介: 乔志刚, 男, 硕士生, 主要从事金属水三相点瓶复现系统方面的研究。

导师简介: 吴琦, 男, 教授, 博士生导师, 博士, 主要从事海洋传感器方面的研究。

统控制原理图和金属水三相点瓶实物图。研究采用小型化金属水三相点瓶、利用高纯水自发相变原理、采用基于半导体帕尔贴效应的热电冷却器 (TEC) 和温度控制电路实现了对水三相点的复现和保持。利用灵敏度较高的热敏电阻结合温度检测电路, 实现高纯水相变监测; 利用双热电阻和 TEC 构成闭环控制, 根据反馈电阻的温度差, 研究高纯水相变对制冷量需求, 并建立三相点瓶制冷系统热力学模型, 合理调节 TEC 的驱动功率, 实现了水三相点状态的复现和较长时间保持。图 2 中的测量结果表明, 在实验室过程中, 观察到了金属水三相点瓶内的高纯水有明显的过冷现象, 其在液固相变平衡温度 (0 °C) 时仍然没有发生相变, 当其温度达到相变温度 (约 -7.3 °C) 时, 处于

亚稳态的高纯水突然发生相变, 内阱温度骤升, 并且在骤升后趋于稳定, 稳定时间 20 min, 期间波动度 ± 1 mK。分析实验表明, 基于金属水三相点瓶的小型化三相点温度自动复现系统可以实现高纯水的自发相变, 并且能够保持一定时间的稳定温坪状态, 实现对温度传感器的高精度原位温度校准。

研究表明: 将金属水三相点瓶与合理布置的温度监控传感器、TEC 制冷系统和制冷控制电路与算法相结合, 可以自动复现并保持高纯水三相点状态 20 min 及温度波动度 ± 1 mK, 为温度传感器原位校准提供了一个准确、稳定、可持续的环境, 服务于深海、深空高精度温度原位校准。

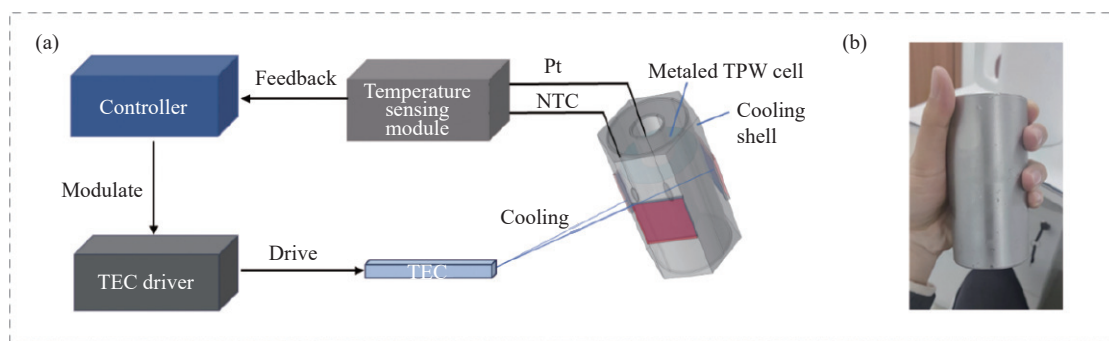


图 1 (a) 金属水三相点瓶自动控制系统示意图 (TEC: 热电制冷器, Pt: 铂电阻, NTC: 负温度系数热敏电阻); (b) 小型化金属水三相点瓶

Fig.1 (a) Schematic diagram of the metal-water triple point cell system (TEC: Thermoelectric cooler, Pt: Platinum resistance, NTC: Negative temperature coefficient thermistor); (b) Miniaturized metal-water triple point cell

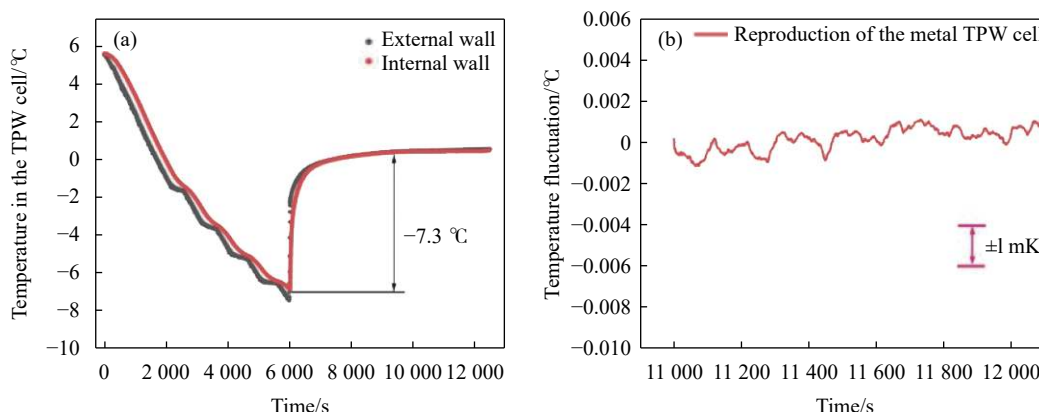


图 2 金属水三相点瓶温度复现。(a) 金属三相点瓶自发相变试验过程 (红线和黑线分别代表瓶内及瓶外温度的变化); (b) 稳定后金属水三相点瓶内温度波动情况

Fig.2 Reproduction of the metal-water triple point temperature in a metal bottle. (a) The spontaneous phase transition experiment of the metal triple point bottle (The red and black lines represent the changes in temperature inside and outside the bottle, respectively); (b) Temperature fluctuations inside the metal-water triple point bottle after stabilization

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Metal water-triple-point automatic reproduction control system for in-situ online calibration of temperature sensors

Qiao Zhigang¹, Gao Dexin¹, Zhang Muzi¹, Zhao Shanshan¹, Wu Jiali¹, Su Juan¹, Chen Shengong², Jing Chao³, Liu Hailing⁴, Yang Bo⁴, Wu Chi^{1,2,3,4}

(1. Institute of Marine Science and Technology, Shandong University, Qingdao 266237, China;

2. Southern Marine Science and Engineering Guangdong Laboratory (Guangzhou), Guangzhou 511458, China;

3. Qingdao Institute of Marine Sensors, Qingdao 266237, China;

4. Aixsensor Co. Ltd., Dezhou 253084, China)

Abstract:

Objective The triple point of water refers to the state where water, ice, and vapor coexist simultaneously, with an equilibrium temperature of 273.16 K (0.01 °C). In the International Temperature Scale, the triple point of water serves as the sole reference point for defining the thermodynamic temperature unit Kelvin, and it is one of the most important fixed points in ITS-90 [1-2]. The thermodynamic temperature reproduction of water's triple point is crucial for practical temperature measurements [3]. The reproduction of water's triple point is achieved by freezing an ice mantle inside a triple point of water cell. Widely used in the ITS-90 guidelines are triple point of water cells with borosilicate glass or fused silica shells. Traditional reproduction methods include the ice-salt mixture cooling method, dry ice cooling method, and liquid nitrogen cooling method. These methods all require the cooling of the triple point of water cell using dry ice, liquid nitrogen, or other cryogenic media, followed by freezing the high-purity water inside the cell and then storing it in an ice bath. While these traditional methods offer high reproduction accuracy and good results, they are complex, operationally difficult, and demand high standards for operators and the environment, making them inconvenient for on-site calibration and integrated applications [2-3]. Addressing the limitations of traditional triple point of water cells and reproduction methods for in-situ applications, such as the on-site calibration of temperature sensors in the deep sea, this paper investigates a miniaturized triple point reproduction control system suitable for the automatic calibration of temperature sensors, based on a self-developed miniature metal water triple point cell.

Methods This control system utilizes the principle of spontaneous phase transition of high-purity water in a metal water triple point container, combined with a thermoelectric cooler (TEC) based on the semiconductor Peltier effect and a temperature control circuit, to achieve the automatic reproduction and maintenance of the water triple point. Temperature phase transition monitoring is achieved through the use of thermistors and temperature detection circuits. By employing a dual thermistor setup and TEC in a closed-loop control, the system adjusts the driving power of the TEC based on the temperature difference detected by the feedback resistors, thereby realizing the automatic reproduction and maintenance of the water triple point.

Results and Discussions Figures 1(a) and (b) respectively illustrate the control schematic of the automatic

reproduction system for the metal water triple point bottle and a photograph of the actual metal water triple point bottle. The research employed a miniaturized metal water triple point bottle, utilizing the principle of spontaneous phase transition of high-purity water, along with a thermoelectric cooler (TEC) based on the semiconductor Peltier effect and a temperature control circuit, to achieve the reproduction and maintenance of the water triple point. High sensitivity thermistors combined with a temperature detection circuit were used for monitoring the phase transition of high-purity water. A closed-loop control consisting of dual thermistors and the TEC was utilized. Based on the temperature difference detected by the feedback resistors, the study investigated the cooling demand of the high-purity water phase transition and established a thermodynamic model for the triple point bottle cooling system. By appropriately adjusting the TEC's driving power, the state of the water triple point was reproduced and maintained for an extended period. The measurement results in Figure 2 indicate that, significant supercooling of the high-purity water inside the metal water triple point bottle was observed. It remained unfrozen at the liquid-solid phase equilibrium temperature ($0\text{ }^{\circ}\text{C}$) and suddenly underwent a phase transition when the temperature reached the transition temperature (approximately $-7.3\text{ }^{\circ}\text{C}$), causing a rapid increase in the internal trap temperature, which then stabilized, with a stability duration of 20 minutes and a temperature fluctuation of $\pm 1\text{ mK}$. The analysis of the experiment demonstrates that the miniaturized triple point temperature automatic reproduction control system based on the metal water triple point bottle can achieve spontaneous phase transition of high-purity water and maintain a stable temperature plateau for a certain period, facilitating high-precision in-situ temperature calibration of temperature sensors.

Conclusions This study indicates that combining the metal water triple point bottle with properly arranged temperature monitoring sensors, a TEC cooling system, and a refrigeration control circuit and algorithm can automatically reproduce and maintain the high-purity water triple point state for 20 minutes, with a temperature fluctuation of $\pm 1\text{ mK}$. This provides an accurate, stable, and sustainable environment for in-situ calibration of temperature sensors, serving high-precision in-situ temperature calibration in deep-sea and deep-space environments.

Key words: metal-water triple point bottle; in-situ automatic calibration device; method for automatic reproduction of temperature plateau

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