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Two decades of spectrophotometric pH measurements along the Atlantic GOSHIP-A25 section

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Between the years 2002 and 2023, seawater pH was determined in more than 20,000 samples within the biennial Franco-Spanish framework of oceanic observations in the North Atlantic (OVIDE-BOCATS), during 11 cruises along the transoceanic A25 line of the GO-SHIP programme. The OVIDE-BOCATS pH measurements were regularly carried out using a spectrophotometric technique based on the pioneering article by Clayton and Byrne (1993), which allows for the total scale pH (pH_{τ}) determination at 25°C by using a seawater-prepared solution of *m*-cresol (Sigma Aldrich; 2mM) dye or indicator. Although this methodology provides very high reproducibility (<0.001 pH units), it has been updated since 2007 (Yao et al., 2007) in various articles to improve the problems associated with indicator impurities. Despite this, the same methodology has been used throughout the OVIDE-BOCATS series, but during the oceanographic expeditions of 2018, 2021 and 2023, samples have been replicated using the habitual pH_T determination with a non-purified indicator, and a purified indicator, not commercially available. For the purified indicator samples, we determined two different pH_T values following the functions proposed by Liu et al. (2011) and DeGrandpre et al. (2014) that allow obtaining the pH_T from the absorbances. Beyond the comparison of the resulting pH_T values between the use of pure and impure indicators, we also tested the differences that arise when applying the correction for the effect of impurities in pH_T measurement proposed by Douglas and Byrne (2017). Our methodology has also been contrasted against reference materials (TRIS buffers) determining an average bias of +0.006 ± 0.003 pH units. We found the same bias when comparing replicate samples measured with pure and impure dyes, thus attributing the bias to the use of an unpurified dye. Our results suggest that the best correction using the TRIS buffer is obtained in samples measured with purified dye and using the equation of DeGrandpre et al. (2014). These experiments, carried out on more than 178 samples, allowed us to correct the bias and standardize the entire series of two decades of pH measurements in the North Atlantic.