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Improving the accuracy of helium and neon measurements in ocean waters

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The helium and neon solubility disequilibria across the ocean-atmosphere interface serve to study the physics of air-sea gas exchange, but the effect is small so that only high-accuracy data give useful results. Weak points are measurement calibration and uncertain solubility equilibrium values in seawater, especially so for the helium isotopes.

Calibration: The classical calibration of mass spectrometric helium and neon measurements uses aliquots of atmospheric air, which is convenient but limited in accuracy and long-term stability. Our alternative is to use water samples equilibrated with undisturbed air, so that their mass can be converted into equivalent volumes of air using a solubility function. In this way, the samples allow a precise recalibration of the air aliquots. A bias relative to regular samples is excluded because the equilibrated water is subjected to exactly the same treatment. The equilibration unit has a water capacity of 4.5 liters. The water is circulated over exchange mats, yielding full air-water equilibrium within two hours, and temperature, pressure, and humidity are precisely controlled. In consequence, we achieve solubility equilibrium within ± 0.03%, so that high accuracy and long-term stability of the calibration are guaranteed. The solubility equilibrium values are more uncertain, but a biased value will only introduce a common shift to the data, i.e. it will not affect the internal consistency of the calibration. The new calibration mode will also enable efficient intercalibration between laboratories.

Solubility determination and sampling procedures: We shall use the equilibration unit to obtain solubility functions of helium and neon in distilled water and seawater with a projected accuracy of ± 0.2%. One measure to achieve this is to compare the mass spectrometric signals of the water and the air phase directly. In this context, we developed a procedure to sample water into glass ampoules to be flame-sealed. They are filled about half, which means that the gas in the head space can directly be admitted into the mass spectrometer, because only about 1% of the helium and neon remains in solution. The uncertainty of the helium and neon concentrations introduced by the procedure does not exceed ± 0.05% and blanks are about negligible. The device is simple and handling fast. Experience on a cruise into the tropical Atlantic has proven that the sampling procedure can be applied reliably in the field. We also devised a way to transfer air samples into identical ampoules.