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# A method to measure the density of seawater accurately to the level of $10^{-6}$

Hannes Schmidt<sup>1</sup>, Henning Wolf<sup>1</sup> and Egon Hassel<sup>2</sup>

<sup>1</sup> Physikalisch-Technische Bundesanstalt, Bundesallee 100, 38116 Braunschweig, Germany

<sup>2</sup> Lehrstuhl für Technische Thermodynamik, Universität Rostock, Albert-Einstein-Straße 2, 18051 Rostock, Germany

E-mail: [henning.wolf@ptb.de](mailto:henning.wolf@ptb.de)

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## Abstract

A substitution method to measure seawater density relative to pure water density using vibrating tube densimeters was realized and validated. Standard uncertainties of  $1 \text{ g m}^{-3}$  at atmospheric pressure,  $10 \text{ g m}^{-3}$  up to 10 MPa, and  $20 \text{ g m}^{-3}$  to 65 MPa in the temperature range of  $5^\circ\text{C}$  to  $35^\circ\text{C}$  and for salt contents up to  $35 \text{ g kg}^{-1}$  were achieved. The realization was validated by comparison measurements with a hydrostatic weighing apparatus for atmospheric pressure. For high pressures, literature values of seawater compressibility were compared with substitution measurements of the realized apparatus.

Keywords: seawater, high precision density measurement, substitution method, vibrating tube densimeter, high pressure adjustment

(Some figures may appear in colour only in the online journal)

## 1. Introduction

### 1.1. Traceability of practical salinity

In times of rapid climate change it is essential to have a detailed description of interactions between the systems affecting climate. The oceans act as a storage and transport system of heat and  $\text{CO}_2$  and are closely linked to climate—the condition of one affects the other. Temperature distribution on Earth is strongly influenced by heat transport caused by deep-sea currents. Their driving forces are density gradients that are in turn caused by temperature and salt content gradients. For a better understanding and more precise modelling of oceanic currents, accurate knowledge of those seawater properties is thus mandatory. An overview is given in the review papers of Feistel *et al* [1] and Pawlowicz *et al* [2].

Values of *in situ* ocean density are usually determined from measurements of salt content, temperature, and pressure using equations of state. The salt content, which is characterized by the quantity salinity<sup>3</sup>, is calculated from electrical conductance measurements of seawater. The procedure for measuring the conductances and the relation to salinity are defined by

the Practical Salinity Scale PSS-78, which was established and adopted by the Joint Panel on Oceanographic Tables and Standards [3] in 1978.

According to the PSS-78 the calibration of conductance meters used for the determination of salt content via practical salinity is performed by using so-called standard seawater, which is produced from natural seawater of the Atlantic Ocean [4], as reference liquid. This bears a certain risk of inconsistency in the long-term, since the ocean is a dynamic system and the composition of standard seawater may change with time. Even when standard seawater is regularly collected, bottled and stored for decades, there is a risk that the bottled seawater may change with time, since interactions of the seawater with borosilicate glass used for storage have been detected [4] resulting in possible changes of its salt composition.

To overcome any possible inconsistencies, Seitz *et al* [5] proposed the establishment of the traceability of salinity to density by performing direct density measurements on standard seawater with well-known salinities. Since density is a derived quantity of the International System of Units (SI), the traceability of salinity measurements performed in this way no longer depends on the stability of standard seawater. Furthermore, density is a major target quantity for the physical description of oceanic currents. The traceability of

<sup>3</sup> Practical salinity is typically used as a unitless quantity but is approximately equivalent to units of grams dissolved salt per kilogram seawater.

the conductance measurements directly to density has the advantage of a shorter traceability chain while common conductance measurements can be used further. Density can be measured in the full ranges of temperature and pressure, therefore guaranteeing traceability at all temperatures and pressures occurring in the oceans, whereas the traditional PSS-78 method only gives a well-defined calibration at one temperature at standard pressure. Furthermore, density measurement includes seawater components that do not contribute to the conductivity, like the non-conducting silicates.

A disadvantage of the traceability to density is the density sensitivity of salinity; density shows an increase of only 3% when comparing pure water to seawater, whereas salinity increases from  $0 \text{ g kg}^{-1}$  to  $35 \text{ g kg}^{-1}$ , which is corresponding to a conductivity range from  $0.055 \text{ }\mu\text{S cm}^{-1}$  to  $42 \text{ mS cm}^{-1}$ . To trace the salinity of seawater accurately to the order of  $10^{-5}$ , the density therefore has to be measured with an uncertainty at the level of  $10^{-6}$ .

## 1.2. State-of-the-art densimetry

**1.2.1. Atmospheric pressure.** Hydrostatic weighing apparatuses are known to be the most accurate densimeters for determining the density of liquids. They usually use a sinker, which is connected to a balance by a suspension. This leads to some difficulties that are increased by the properties of seawater. The liquid to be measured is in some way open to the environment. That leads to water evaporating, thereby enriching the salt content and changing the density. Moreover, a well-known problem of the hydrostatic weighing apparatus is the poor reproducibility of the meniscus arising at the penetration point of the suspension through the liquid's surface. The problem is well-known in measurements of water. Furthermore, a severe problem is the sinker material. Nowadays sinkers are often made of silicon, which is well characterized and mostly stable. But there is a high risk of corrosion in seawater even when the silicon is passivated by a silicon dioxide layer, see section 2.2.3 for details.

As long ago as 1971 the use of vibrating tube densimeters (VTDs) for seawater was proposed by Kremling [6]. Advantages compared to other types of densimeters are the very small amount of liquid needed per measurement, the easy replacement of fluids by flushing, the minimization of evaporation, and the quick measurements. A disadvantage is the high measurement uncertainty of  $0.01 \text{ kg m}^{-3}$  to  $0.02 \text{ kg m}^{-3}$ .

Wolf [7] proposed measurements with VTDs using a substitution method. He pointed out that substitution minimizes systematic uncertainty contributions, most drifting effects, and thus overall uncertainty. He also showed some substitution measurements of seawater at atmospheric pressure using ultrapure water as a reference. The liquids were filled into the VTDs using syringes, which were changed manually to alternate seawater and pure water. Using manually operated syringes increases the risk of influences from evaporation and handling. An automated filling procedure was therefore expected to yield better repeatability and reproducibility. Wolf estimated a standard uncertainty of about  $0.001 \text{ kg m}^{-3}$ . Measurements of seawater density at the level of  $10^{-6}$  thus

seemed to be possible, if this method is used with an automated filling procedure.

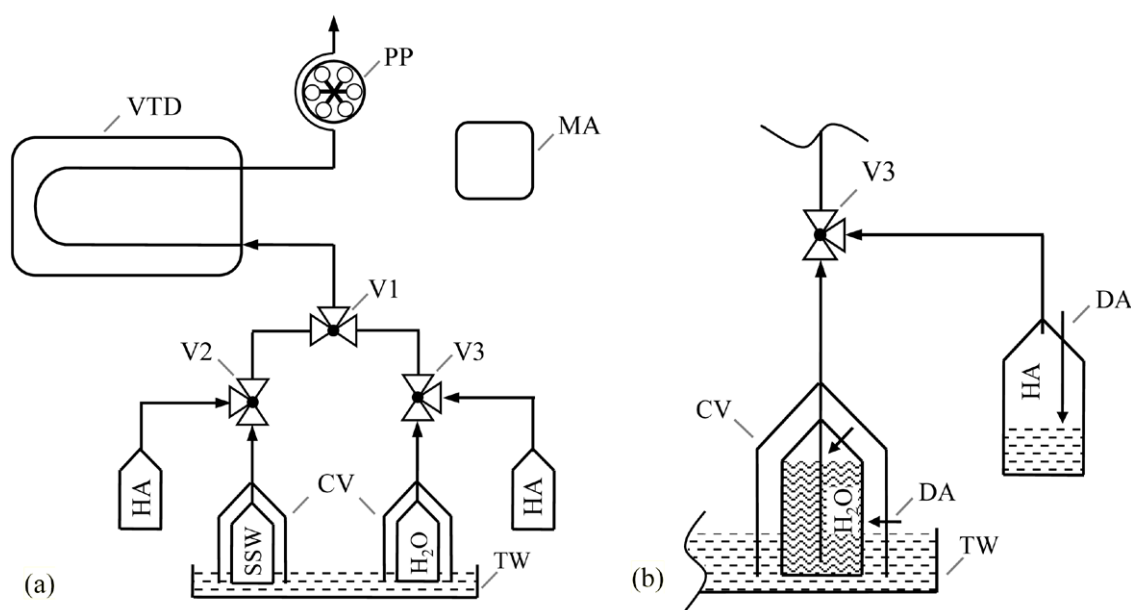
**1.2.2. High pressure.** Magnetic levitation densimeters are known to be the most accurate primary densimeters for high pressures. High accuracy versions use two sinkers to decrease uncertainty contributions from the magnetic coupling of the sinkers and balance. Reported uncertainties of existing installations vary, since the realizations of the sinker installation are different. Mostly the achievable uncertainty was reported to be at least  $100 \times 10^{-6}$  at higher pressures, e.g. by Wagner and Kleinrahm [8] and McLinden and Lösch-Will [9]. Kayukawa *et al* [10] developed an improved design for high pressures, validated it at atmospheric pressure, and reported a standard uncertainty of  $2.3 \times 10^{-6}$ . They used one sinker made of silicon and another made of germanium. Kayukawa *et al* also undertook measurements on water and reported air bubbles disturbing the measurements. If seawater is filled in such a densimeter, there is also a high risk of evaporation that increases the salt content and thus the density, since filling is performed in vacuum. As already mentioned, there is also a high risk of the corrosion of silicon in seawater.

Disadvantages of magnetic float densimeters [11] are similar to those of magnetic levitation densimeters, since the measurement principle is similar.

Vibrating tube densimeters are used for measurements of density over a wide range of temperatures and pressures. Advantages of measurements using high pressure VTDs are similar to those of atmospheric pressure VTDs as described above. A disadvantage is the decrease in repeatability, because commercially available high pressure VTDs are not equipped with a reference oscillator. Especially temperature hysteresis effects on the vibrating tube material are therefore not compensated for. This effect can be overcome using the substitution method. Another problem is the lack of reference substances with well-known densities at high pressures needed for adjustment. This also hinders the validation of adjustment approaches, which have been developed for more than 20 years. Using reference substances with high uncertainties bears an additional risk of nonlinearity that is not overcome by the substitution method.

## 1.3. Scope

In this paper, we present the realization of a substitution method using a VTD to measure seawater density at atmospheric pressure overcoming the disadvantages of a manual substitution measurement. A filling system was especially designed for replacing water and seawater using the smallest amounts of liquid without evaporation, therefore overcoming all disadvantages of syringe-based filling and also sample-changer filling measurements. The uncertainty budget of a substitution measurement of seawater using ultrapure water as a reference was analysed and a validation by comparison measurements with hydrostatic weighing apparatus was performed. Overall uncertainty was evaluated to be  $2 \times 10^{-6}$  in the temperature range of  $5 \text{ }^{\circ}\text{C}$  to  $35 \text{ }^{\circ}\text{C}$ . The method can hence be used to carry out highly accurate, traceable measurements of seawater density.



**Figure 1.** Set-up to realize the substitution method for atmospheric pressure. (a) Scheme of the set-up. Rinsing is supported using bubbles of saturated humid air. (b) Scheme of the bottle connections of water reference side. Bottle connections of the seawater sample side are analogous. VTD—Densimeter, PP—Peristaltic pump, V1—Liquid switching valve, V2/V3—Air switching valves, SSW—(Standard) Seawater, H<sub>2</sub>O—Ultrapure water, HA—Humid air, DA—Dry air, CV—Cover, TW—Tap water, MA—Manometer. The arrows indicate flow direction in capillary tubes.

The presented realization can be used to establish the traceability of the practical salinity of standard seawater (SSW) directly to density, thereby including the thermophysical property thermal expansion. Any changes in the SSW that contribute to the density can therefore be identified. This prevents inconsistencies in the determination of salinity over long periods. Ocean currents transporting heat in the deep sea over very long distances can thus be described without inconsistencies in the long term. This helps the use of those oceanic flow models that simulate these currents for the prediction of climate.

We also present the realization of a substitution method using a VTD for high pressures. For this purpose, an adjustment approach was developed and validated that overcomes the lack of reference substances and improves linearity for seawater measurements. The substitution method at high pressures is validated using compressibility measurements of seawater. The uncertainty budget was analysed and the overall expanded uncertainty was calculated to be  $20 \times 10^{-6}$  up to 10 MPa and  $40 \times 10^{-6}$  to 65 MPa in the temperature range of 5 °C to 35 °C. The realization can be used to extend the traceability of salinity to density into the range of high pressures, thereby including the compressibility properties of the standard seawater.

## 2. Realization for atmospheric pressure

### 2.1. Method

**2.1.1. Apparatus.** The density measuring apparatus consists of a VTD with a specially developed filling system, since for the substitution method, the reference and sample liquids have to be cleanly replaced before each particular measurement. The filling system is designed to replace one liquid by

another; through the use of air bubbles in the replacement process, residua of the replaced liquid are minimized. The set-up is shown schematically in figure 1. The bottle with the reference liquid (ultrapure water) is placed together with the bottle with the sample liquid (seawater) in a container filled with tap water to stabilize both liquids at the same temperature and minimize impact from the environment. The bottles have a small orifice for air to allow pressure equilibration when the temperature is changed or liquid is pumped out of the bottle. Through covers over the bottles, the air for pressure equilibration is kept saturated with water. Non-saturated air would take water molecules from the seawater and cause an increase in the density. The covers have a small orifice towards the surrounding environment.

Special attention was paid to the replacement of liquids in the VTD. The amount of liquid for rinsing the tubes was reduced to a minimum. Concurrently the efficiency of the rinsing was increased. This was achieved by adding air bubbles for flushing. Next to the bottles (SSW/H<sub>2</sub>O) switching valves (V2/V3) are installed to inject air in the form of small bubbles into the filling system. The injected bubbles pass into the particular liquid through the tubing and the valve to switch between the liquids (V1). Since water and seawater have a high surface tension, air bubbles are forced to fill a large part of the cross section of the tubes and thus help to flush away the water located near to the walls and in the dead space of the valves and joints with different diameters. Air bubbles are taken from bottles filled with water-saturated air (HA) to avoid the enrichment of salt due to the evaporation of water into these bubbles. The peristaltic pump (PP) for the transportation of air and liquids was positioned behind the densimeter to avoid any influence of the tubing, since peristaltic materials often absorb water and may interact with seawater.

Tubing material used between the bottles (SSW/H<sub>2</sub>O) and the densimeter (VTD) is made of PTFE and stainless steel. The tube inner diameters are around 1.5 mm, respectively. The valves are made of PEEK. The VTD is a DMA 5000 M supplied by Anton Paar GmbH, Austria. The atmospheric pressure was monitored by a PTU 300 manometer (MA) supplied by Vaisala, Finland.

**2.1.2. Materials.** The raw material for the ultrapure water that is used as a reference liquid for the substitution measurements was tap water from Braunschweig, Germany. It was deionized using reverse osmotic apparatus and filtered by a 0.2 µm filter. Its purity was monitored by measuring the conductivity, which was always significantly lower than 0.1 µS cm<sup>-1</sup> at 20 °C to 25 °C at the outlet of the reverse osmotic apparatus. To obtain air-free water, the deionized water was subsequently boiled for half an hour, filled in borosilicate bottles, and sealed in a hot state. Bottled water was used within a week.

For determining the repeatability of the substitution method, measurements were undertaken using natural seawater from the Atlantic Ocean with a salinity of 35, which was filtered by a 0.45 µm filter.

For the validation of the substitution method, comparison measurements with a hydrostatic weighing apparatus were performed, so that greater amounts of liquids with defined densities were needed, see section 2.2.3. In this case aqueous sodium chloride solutions were therefore used as sample liquids. The solutions were (i) premixed to target densities representing the density range of seawater, filtered, and filled in 2 L bottles, (ii) slowly stirred for 8 h in closed bottles to homogenize the liquid without heating, and (iii) kept at 20 °C for at least 24 h in closed bottles without stirring. Step (iii) was conducted, as the liquid was found to be oversaturated with air after step (ii). Small air bubbles were regularly found after step (iii) and eliminated by moderate mechanical shocks. Samples of these solutions were filled under water-saturated air to minimize evaporation and then measured using the VTD as well as the hydrostatic weighing apparatus.

**2.1.3. Filling procedure.** The procedure for filling the measured material into the VTD was optimized to reach a high repeatability of the measurements. This can be done by avoiding large temperature changes during the rinsing and filling process and by keeping the unavoidable temperature changes for the water and seawater fillings as similar as possible. As a consequence, the procedure was optimized for small rinsing and filling volumes and for a high repeatability of the rinsing and filling process.

The best results could be achieved with the following procedure for the replacement of one liquid by the other: a replacement consists of five particular fillings, each consisting of (i) a series of air bubbles in the liquid to be measured followed by (ii) a fixed amount of the liquid to be measured. The series of bubbles is generated by opening and closing a valve connected to water-saturated air. Since this valve needs a certain time to operate, a flow rate of 3 ml min<sup>-1</sup> is used during this time. The particular volume of bubbles and liquid is transported at a flow rate of 20 ml min<sup>-1</sup> to prevent sticking of the air bubbles.

Because of remaining liquid deposits in dead spaces of the valves or tube joints with different diameters, which are still not flushed away by the use of air bubbles, a certain waiting time between the particular fillings was introduced to enable diffusion and dilution processes. Since after each further flush the diffusion and dilution processes take longer to have a significant effect, the waiting time increases starting from 4.5 min and ending at 15 min before the last particular filling. To reach a temperature equilibrium, a waiting time of 10 min follows the last particular filling before the VTD is ready for measuring. The total time for this replacement procedure is approximately 60 min. The total liquid volume for one replacement is 10 ml.

**2.1.4. Measuring procedure.** A thermal equilibration time of at least 8 h at measurement temperature precedes every measurement series to stabilize the VTD. The measuring procedure itself consists of at least eight alternative measurements of water (reference) and seawater (sample), whereby the reference liquid is measured first and last. The particular density of a filling is measured ten times independently. The averaging of these measurements is done by the VTD software of the manufacturer. The total measurement time for one substitution measurement with ten particular substitution results including the thermal equilibration time is 30 h.

**2.1.5. Adjustment and calibration.** The densimeter offers a basic adjustment by the manufacturer. It additionally offers a simple two-point adjustment at 20 °C using air and water to eliminate drifts. This adjustment was performed regularly between any changes of measurement temperatures.

Temperature measurement was carried out using the internal thermometer of the densimeter. This thermometer was calibrated using platinum resistance sensors (PT-100) that were connected to an Anton Paar MKT50. These sensors were calibrated at the *Physikalisch-Technische Bundesanstalt* (PTB). To measure the temperatures in both legs and the temperature gradient along the vibrating tube to the connecting ports, the PT-100 were placed directly inside both sides of the vibrating tube at different positions. Overall standard uncertainty of the calibration is 2.5 mK.

The manometer was calibrated at PTB. Since the sensitivity of density on pressure is relatively small, the calibration correction was not used. The standard uncertainty in pressure was therefore increased to 200 Pa.

**2.1.6. Calculation.** The result of a substitution measurement performed is calculated using the difference equation:

$$\rho_{\text{subs}} = \rho_{\text{ref}} - \rho_{\text{ref,mes}} + \rho_{\text{s,mes}} \quad (1)$$

where  $\rho_{\text{subs}}$  and  $\rho_{\text{s,mes}}$  are the substitution density and the measured density of the seawater sample, respectively,  $\rho_{\text{ref}}$  is the known reference density of the pure water reference, the calculation of which is described in appendix A.2, and  $\rho_{\text{ref,mes}}$  is the measured density of the pure water reference. An alternative equation to calculate the result of a substitution measurement would be:

$$\rho_{\text{subs}} = \frac{\rho_{\text{ref}}}{\rho_{\text{ref,mes}}} \cdot \rho_{\text{s,mes}} \quad (2)$$

Both equations give very similar results, since the relative difference between the densities of pure water and seawater is small. The mean deviation is within  $0.0002 \text{ kg m}^{-3}$  for seawater with a salinity of 35. For lower salinities the deviation decreases proportionally to the density difference of seawater and pure water.

One substitution measurement consists of multiple measurements of pure water and seawater, which are each measured alternately. To increase the accuracy of the substitution, the measurement values of the water reference were interpolated linearly to the specific time of the seawater sample measurement. For this interpolation only the two adjacently preceding and following water measurement values are used.

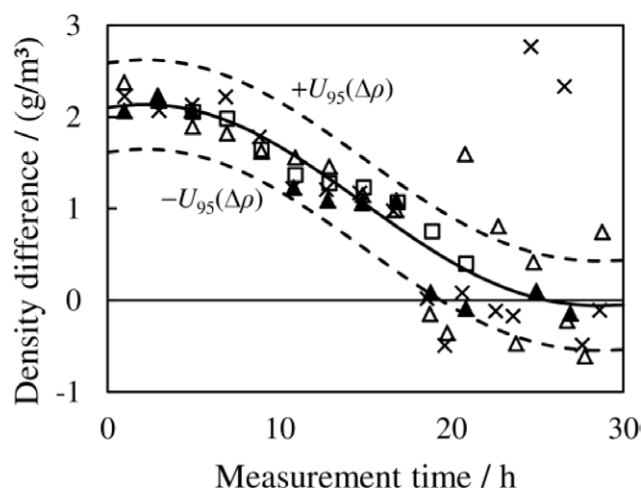
**2.1.7. Aeration of bottled reference water.** The reference water used for the measurements is bottled in hot state after boiling. The bottles used have a filling volume of approximately 250 ml. We always filled a liquid volume of about 225 ml; the remaining 25 ml volume consequently consists of air and water vapour. At the moment of sealing the bottle, the water temperature is near the boiling temperature. Water vapour consequently replaces most of the air in the bottle. After cooling down the sealed bottle to  $20^\circ\text{C}$ , the water vapour pressure is decreased to 2300 Pa. The partial pressure of the remaining air determines the aeration of the liquid water. The residual pressure is therefore a direct measure of the aeration of water, and the filling temperature is (indirectly) another, since it determines the pressure after cooling down.

The relationship between the filling temperature and the residual pressure is estimated by applying the ideal gas law, liquid water density-temperature dependence, and Henry's law. We used the values of Henry's constants of nitrogen, oxygen, argon and carbon dioxide given by Harvey *et al* [12] to calculate the number of molecules absorbed into the liquid water.

Two methods were consequently applied to estimate the aeration of the bottled water. Firstly we measured the temperature by placing a PT-100 sensor into the water immediately after filling to find the temperature at the moment of sealing the bottle. This temperature was in the range  $90^\circ\text{C}$  to  $94^\circ\text{C}$ . Then we calculated the corresponding residual pressure range using the relationship, which is 27800 Pa to 18500 Pa, respectively. This corresponds approximately to an aeration of 27% to 17%, respectively, if full aeration is defined at 101325 Pa.

Secondly we measured the residual pressure by sticking a syringe, which is mounted on a quartz pressure sensor, through the seal of the bottle. The measurement value was corrected for the dead volumes of syringe and sensor. The residual pressures measured are in the range 16500 Pa to 26500 Pa. This corresponds approximately to an aeration of 16% to 26%, respectively, thereby confirming the first approach. Additionally, we checked the seal for tightness by measuring the residual pressure in sealed bottles after two weeks; no significant pressure increase was detected.

Finally the aeration of bottled water used for seawater substitution measurements is estimated to be 20% with a standard uncertainty of 5%.



**Figure 2.** Density difference due to aeration of reference water during the time of a substitution measurement at  $20^\circ\text{C}$ .  $U_{95}(\Delta\rho)$ —estimated expanded uncertainty of the approximation derived from the four measurements ( $\square$ ,  $\triangle$ , and  $\times$ ).

**2.1.8. Aeration of reference water during measurement.** When water is taken from the bottle during the filling of the densimeter, air flows into the emptied space in the bottle due to pressure equilibration. The water consequently aerates during the substitution measurement. To quantify this effect in terms of density, we measured the density of 20% aerated (reference) water as used for the substitution measurements against a fully aerated water, thereby applying the same procedure and realisation as for the substitution measurements. Fully aerated water is expected to have constant density throughout the measurement time.

The water with full aeration was produced by: (i) cooling-down boiled pure water in the 250 ml bottle to  $20^\circ\text{C}$ , (ii) shaking the bottle for at least 5 min, and (iii) equilibration of the bottled water for at least 24 h. The latter step was necessary, since we found the water to be oversaturated; micro-bubbles caused high scattering during the first measurements.

The measured density difference of the deaerated and fully aerated water at  $20^\circ\text{C}$  is shown in figure 2. Four measurements were conducted. The initial aeration of the reference water was estimated to be 20% at  $20^\circ\text{C}$  in the previous section. The density effect of the remaining 80% aeration derived from the measurements is  $-2.1 \text{ g m}^{-3}$ . This results in  $-2.6 \text{ g m}^{-3}$  for 100% aeration, which is in good agreement with the value of  $-2.44 \text{ g m}^{-3}$  stated by Harvey *et al* [12]. This difference decreases after some measurements, since the degassed water becomes more aerated. The aeration is driven by diffusion, which is forced through the water removal, since the water level falls. To minimize this effect, the water is always taken from the bottom of the bottle. The density of the deaerated water converges the density of the fully aerated water after 20 h, which is also the measurement time of a substitution measurement with 10 particular results. When both liquids are fully aerated, the scatter increases largely. We assume that micro-bubbles can arise more numerous in the tubes and are no longer dissolved by the deaerated water. A substitution measurement is therefore finished within 20 h, where the correction is unaffected by scattering.

Micro-bubbles can also arise, if temperature and pressure are changed, thereby causing significant changes in the water density at the level of  $10^{-6}$ . This is the main problem in using fully aerated water for substitution measurements at temperatures higher than 20 °C. Additionally, the uncertainty of the reference density values corrected for aeration is significantly increased.

The correction for aeration that was derived from the measurements is also given in figure 2. This correction was applied to the measured reference water densities before calculation of the seawater substitution results using (1). If substitution measurements at temperatures different from 20 °C were corrected for aeration, the correction values were converted to the density effect at the corresponding temperature.

We estimate the overall standard uncertainty of our measurements concerning the determination of the aeration to be 10%. This includes also the uncertainty of initial aeration determination described in the previous section. The expanded uncertainty given in figure 2 therefore corresponds to around 20% in aeration at 20 °C.

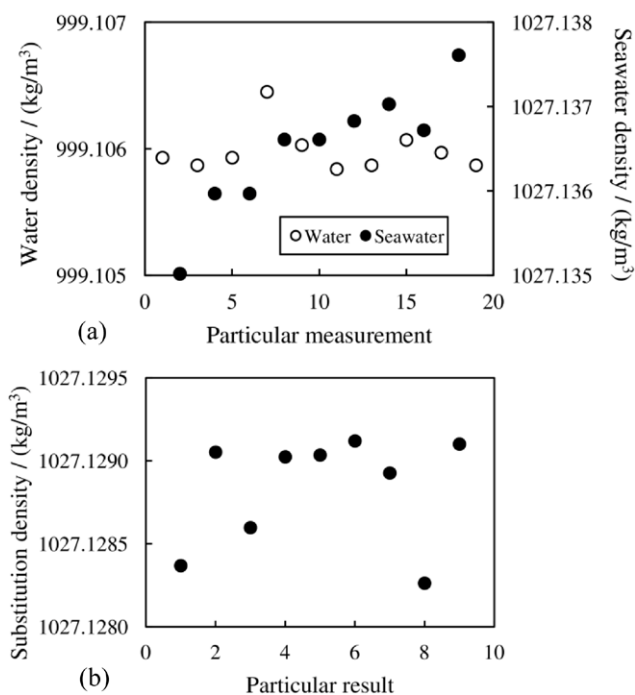
**2.1.9. Isotopic composition of bottled reference water.** For the preparation of the reference water, tap water from Braunschweig was used. The isotopic composition of tap water from Braunschweig has been measured several times since 1985. The resulting data confirm stability of the deuterium and oxygen-18 isotopic abundances for this time. Such measurements were performed as well on tap water as on de-ionised water and water degassed by boiling. No significant deviations were found between these water samples. The data are given in appendix A.2.

## 2.2. Results

**2.2.1. Repeatability.** A typical measurement showing the densimeter stability during a substitution measurement is shown in figure 3. The measurement with nine particular results took 20h. Within this time the pure water density values remained constant whereas the seawater density values drifted by  $2 \text{ g m}^{-3}$ . The scattering of the particular substitution results is within  $1 \text{ g m}^{-3}$ .

Filtered natural seawater filled in different bottles was measured to determine the repeatability. The results are shown in figure 4. Most of the measurement values could be repeated within  $0.2 \text{ g m}^{-3}$  and all measurement values could be repeated within  $1 \text{ g m}^{-3}$  except one measurement. A repeatability of  $1 \text{ g m}^{-3}$  at a probability of 95% is therefore assigned to the realization. This also includes the repeatability of preparation and bottling of the reference water.

**2.2.2. Uncertainty.** Uncertainty contributions of 10 quantities were considered, thereby separating contributions from our own measurements and equations of state (EOS) from the literature. Table 1 shows the uncertainty budget of a measurement of seawater at 15 °C, which is based on the uncertainty model given in appendix A. The main contributions are from adjustment, reference values, and repeatability, which contribute with about 90% to uncertainty. The overall standard uncertainty is  $0.001 \text{ kg m}^{-3}$ .



**Figure 3.** Substitution measurement of filtered seawater with a salinity of 35 at 15 °C. Measured densities of pure water and seawater (a) and resulting calculated substitution results (b). Measurement time was 19 h.

If a substitution measurement is carried out at a lower salinity, the uncertainty contribution from the adjustment decreases, since the density difference decreases relatively to water density. The dependence of the overall standard uncertainty on practical salinity is therefore given in figure 5. The uncertainty varies between  $0.8 \text{ g m}^{-3}$  and  $1.0 \text{ g m}^{-3}$  in the salinity range of 0 to 35, which is of interest for the salinity traceability.

Since the uncertainty dependence on temperature and aeration is of minor significance in the temperature range of 5 °C to 35 °C, the uncertainty dependence on salinity shown in figure 5 may also be taken for these temperatures.

**2.2.3. Validation.** A comparison measurement with hydrostatic weighing apparatus was performed to validate the realized substitution method and the stated uncertainty. This hydrostatic weighing apparatus is a further development of the apparatus presented by Fehlauer and Wolf [13]. The new apparatus is designed to work in the temperature range from  $-40$  °C to 90 °C under atmospherical pressure. Its sinker is a silicon sphere with a natural silicon dioxide layer and is characterized by mass and density, which was measured using a pressure-of-flotation apparatus [14]. The standard uncertainty of an absolute density measurement at 20 °C is  $\leq 1 \text{ g m}^{-3}$ .

Aqueous sodium chloride solutions were premixed to target densities of  $1025 \text{ kg m}^{-3}$ ,  $1030 \text{ kg m}^{-3}$ , and  $1035 \text{ kg m}^{-3}$ . The target densities were chosen to represent the practical salinities 35, 42, and 48.

During the measurements we recognized that there was certain corrosion of the silicon sphere in the salt water. Thus, the measurement time was reduced to a minimum. The mass

**Table 1.** Uncertainty budget of a substitution measurement of seawater with a salinity of 35.

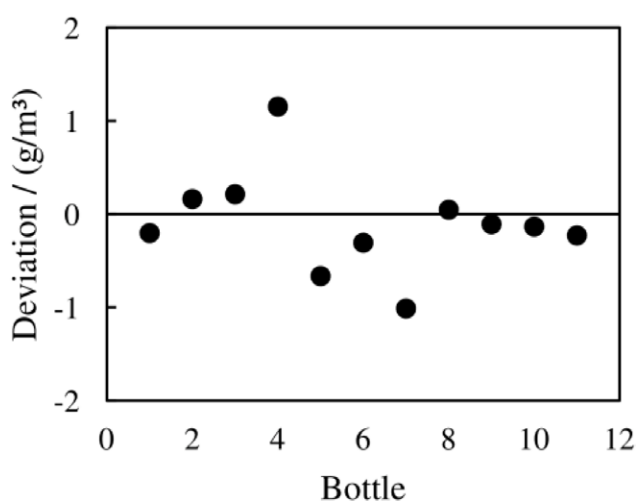
| Quantity                                             | Unit               | Value              | Uncertainty               | Sensitivity <sup>c</sup> | $\nu$           | Significance |
|------------------------------------------------------|--------------------|--------------------|---------------------------|--------------------------|-----------------|--------------|
| Temperature—Measurement                              | K                  | 288.15             | 0.0025                    | $-6.88 \times 10^{-2}$   | $\infty$        | 3%           |
| Pressure—Measurement                                 | Pa                 | 101325             | 200                       | $-2.31 \times 10^{-8}$   | $\infty$        | 0%           |
| [ <sup>18</sup> O]/[ <sup>16</sup> O]—Measurement    | —                  | -0.0085            | $3 \times 10^{-5}$        | $-2.33 \times 10^{-1}$   | $\infty$        | 0%           |
| [ <sup>2</sup> H]/[ <sup>1</sup> H]—Measurement      | —                  | -0.059             | $4 \times 10^{-4}$        | $-1.66 \times 10^{-2}$   | $\infty$        | 0%           |
| Aeration—Reference—Measurement                       | —                  | 0.20               | 0.1                       | $2.85 \times 10^{-3}$    | $\infty$        | 8%           |
| $\Delta\rho$ —Composition—Reference—EOS <sup>a</sup> | kg m <sup>-3</sup> | -0.0030            | -0.00015                  | $9.99 \times 10^{-1}$    | $\infty$        | 2%           |
| $\Delta\rho$ —Aeration—Reference—EOS <sup>a</sup>    | kg m <sup>-3</sup> | -0.0006            | 0.0001                    | 1                        | $\infty$        | 1%           |
| Density—Reference—EOS <sup>a</sup>                   | kg m <sup>-3</sup> | 999.1020           | 0.0005                    | 1                        | $\infty$        | 26%          |
| Repeatability                                        | kg m <sup>-3</sup> | 1025.9593          | 0.0005                    | 1                        | 11              | 26%          |
| Adjustment                                           | kg m <sup>-3</sup> | ref/s <sup>b</sup> | 0.0025 <sup>d</sup>       | ref/s <sup>b</sup>       | 99 <sup>d</sup> | 34%          |
| Effective degrees of freedom                         |                    |                    | 116                       |                          |                 |              |
| Standard uncertainty                                 |                    |                    | 0.0010 kg m <sup>-3</sup> |                          |                 |              |

<sup>a</sup> Uncertainties in equations of state are listed separately if they are significant.

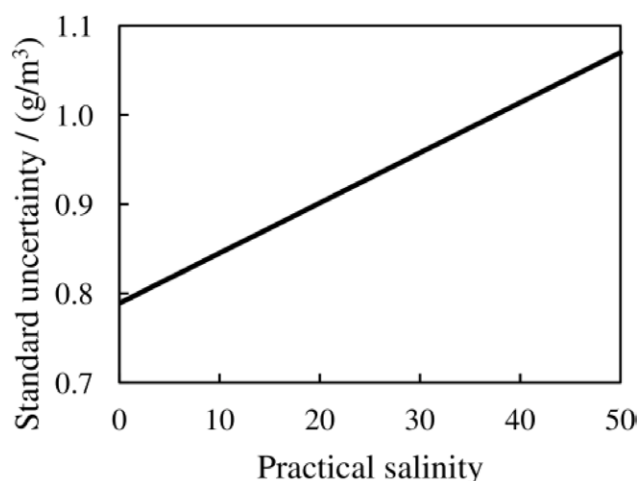
<sup>b</sup> Contribution from adjustment can be separated into contributions of the densities of pure water (ref) and seawater (s), but is summarized for clarity.

<sup>c</sup> Units are kg m<sup>-3</sup>/K, kg m<sup>-3</sup>/Pa, etc.

<sup>d</sup> Values are estimated.

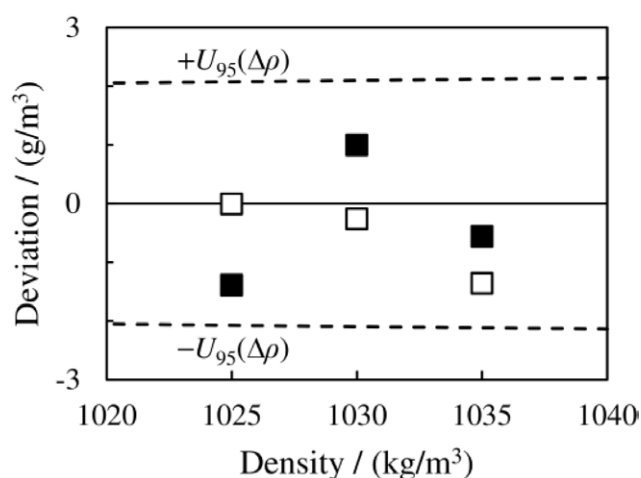


**Figure 4.** Substitution measurements of filtered seawater with a practical salinity of 35 filled in different bottles at 15 °C. Deviation from the mean value of all bottles.



**Figure 5.** Dependence of uncertainty on salinity.

loss after all measurements was 2.3 mg (relative  $9.7 \times 10^{-6}$ ) and the density was unchanged. The resulting drift was corrected and validated by performing additional measurements



**Figure 6.** Deviation of VTD measurements (■ VTD 1 and □ VTD 2) from hydrostatic weighing measurements at 0.1 MPa and 15 °C using samples from the same premixed salt water.  $U_{95}(\Delta\rho)$ —expanded uncertainty of deviations.

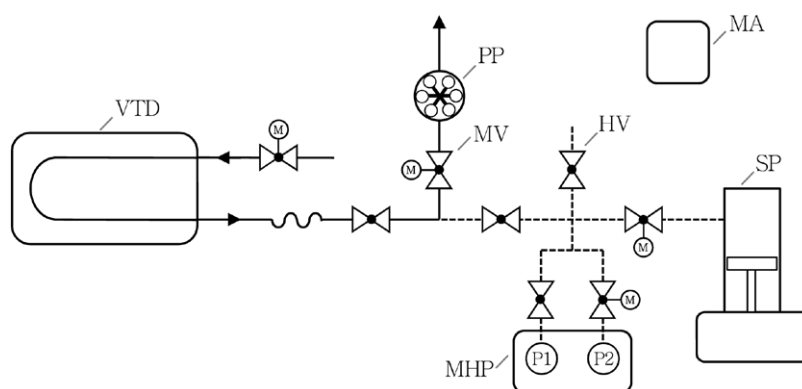
on ultrapure water. Finally the sinker mass and density had been recalibrated for further use, thereby confirming that the sinker density was unchanged.

Results are shown in figure 6. Measurements were performed using two VTDs (Anton Paar DMA 5000M). The measurement temperature 15 °C was chosen to minimize the evaporation of water from the sample. The deviations are fully covered by the uncertainties of the measurements of the hydrostatic weighing and the substitution measurements, which were used to calculate the uncertainty of the deviations. The comparison measurement thus confirms the calculated uncertainty of the realized substitution method.

### 3. Realization for high pressures

#### 3.1. Method

**3.1.1. Apparatus.** The high pressure set-up consists of two parts: the measurement part and the pressurization part, as shown in figure 7. The measurement part including the



**Figure 7.** Set-up of the substitution method realization for high pressure. Parts of the tubing, P1, P2, and SP are filled with oil to prevent corrosion and minimize sample volumes (filled with sample,—filled with oil). A filling system like at atmospheric pressure is used (not shown). VTD—Densimeter, PP—Peristaltic pump, MV—Motor-driven valve, HV—Manual valve, SP—Syringe pump, MA—Manometer for atmospheric pressure, MHP—Manometer for high pressure (P1—Full-range sensor, P2—Low-range sensor).

densimeter is filled with the sample, and the pressurization part, where the pressure is generated and measured, is filled with oil. The latter is to prevent corrosion caused by seawater in the manometer and syringe pump. Furthermore, this construction allows the use of a small sample volume, so that filling requires less liquid. The filling system is the same as that for atmospheric pressure. After the VTD a tube with a length of 1 m is mounted diagonally in altitude to avoid the diffusion and convection of the oil used for pressurization into the measuring part, respectively. All tubing inner diameter is 1 mm resulting in less inner volume and optimized rinsing using air bubbles. A peristaltic pump located at the outlet is used to transport the liquid. The pressure generation is undertaken using a syringe pump. Pressure measurement is performed using two pressure sensors: low-range up to 14 MPa and full-range up to 70 MPa. The valves at the inlet, outlet, and low-range sensor, and also before the syringe pump are driven automatically. To ensure that absolutely no oil diffuses backwards into the measuring part and the outlet tubing remains sufficiently free of oil residuals, a cleaning process using ethanol in addition to water is performed between any series of measurements with new samples.

The pressure is controlled actively. The measurement signal of the manometer was used to drive the syringe pump by a software PID controller. The advantages are independence from the environment (particularly room temperature changes) and less time for pressure line-up than passive control, for example a 5 MPa step is stabilized within 12 min to <1 kPa. The active control improves repeatability and the uncertainty of substitution measurements. The manufacturers and types of components are given in table 2.

**3.1.2. Materials.** The ultrapure water used as a reference liquid was prepared as described in section 2.1.2.

To determine the repeatability, measurements were performed using filtered natural seawater, which was also diluted using ultrapure water to obtain lower salt contents.

The adjustment for atmospheric pressure was performed using *n*-nonane, ultrapure water, and tetrachloroethylene. *n*-Nonane and tetrachloroethylene were obtained from Merck, each having a purity of >99%. In this case their reference

**Table 2.** Description of components of the set-up for high pressures.

| Component               | Manufacturer | Type               |
|-------------------------|--------------|--------------------|
| Densimeter              | Anton Paar   | (DMA 5000M)/DMA HP |
| Manometer               | Vaisala      | PTU300             |
| High pressure manometer | Fluke/DHI    | RPM4 (A14M/A70M)   |
| Syringe pump            | Teledyne     | ISCO 100DM         |

densities were measured, see section 3.2.1. The adjustment for high pressure was performed using only water.

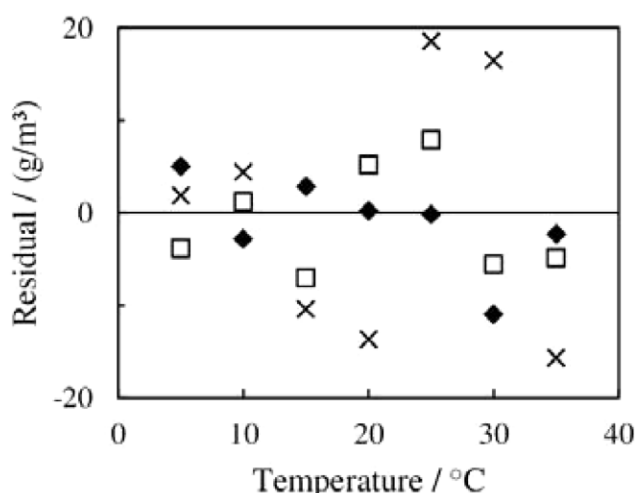
To check the adjustment for high pressures, *n*-nonane and 2,4-dichlorotoluene were used. Both were obtained from Merck, each having purities of >99% and >98%. For the validation of the substitution method for the realisation for atmospheric pressure, aqueous sodium chloride solutions were used that were prepared similarly as described in section 2.1.2. To validate the realization for high pressures, standard seawater recognized by the International Association for the Physical Sciences of the Oceans (IAPSO) obtained from Ocean Scientific International Ltd., Havant, UK was used.

**3.1.3. Filling procedure.** Filling is similar to the procedure described in section 2.1.2, which is undertaken at atmospheric pressure.

**3.1.4. Measuring procedure.** Substitution measurement at high pressures is performed by changing the pressure while the temperature is kept constant. After filling, the pressure is increased in steps starting at 0.3 MPa until the highest pressure of 65 MPa. 0.3 MPa was the minimum pressure found, at which entrapped air in the oil part did not influence the pressure control significantly compared to higher pressures. After stabilization of any pressure value, the density measurement was performed. After measurement of the highest pressure (i) the pressure was decreased and stabilized at 0.3 MPa and (ii) the inlet and outlet valves were opened, so that the pressure is equal to that of the environment. Then the other liquid was filled and measured in the same way. A measurement of one pressure dependent density curve at constant temperature (isotherm) including eight pressure points, filling, and

**Table 3.** Values of properties of the vibrating tube.

| Property                             | Value              | Standard uncertainty | Source |
|--------------------------------------|--------------------|----------------------|--------|
| Outer radius <sup>a</sup> $R$        | 1590 $\mu\text{m}$ | 10 $\mu\text{m}$     | [15]   |
| Wall thickness <sup>a</sup> $\delta$ | 300 $\mu\text{m}$  | 10 $\mu\text{m}$     | [15]   |
| Elastic modulus <sup>a,b</sup> $E$   | 205 GPa            | 10 GPa <sup>c</sup>  | [16]   |
| Poisson's ratio <sup>a,b</sup> $\nu$ | 0.307              | 0.015 <sup>c</sup>   | [16]   |

<sup>a</sup> At reference state 20 °C and 101325 Pa.<sup>b</sup> Assumed to be constant.<sup>c</sup> Values are estimated.**Figure 8.** Residuals of adjustment at atmospheric pressure. Standard deviation is 9 g m<sup>-3</sup>. ♦ *N*-nonane, □ water, and × tetrachloroethylene.

pressure reduction for the next particular filling as described takes eight hours. One substitution isotherm of the sample requires at least one isotherm of the sample and two isotherms of the reference for linear interpolation. Usually five substitution points per pressure are targeted resulting in 11 isotherms.

**3.1.5. Adjustment and calibration.** The high pressure densimeter was adjusted using a new approach given in detail in appendix B. This new approach consists of two stages: the first is the adjustment at atmospheric pressure, the second stage comprises the change of the adjustment coefficients for high pressures. For atmospheric pressure at least three reference fluids are needed to determine the three parameters  $A_0$ ,  $A_2$ , and  $A_4$  ((B.12)–(B.14), appendix B). For the adjustment of the high pressure dependence of the coefficients only one reference fluid is needed ((B.18), appendix B).

The targeted uncertainty determines how the temperature is set throughout and between the stages, since a change of the temperature causes a hysteresis. The highest accuracy is achieved if both stages are passed at constant temperature. In this way, adjustments for specific temperatures result, which can be readjusted simply by a calibration at atmospheric pressure. In our case the effect was neglected and adjustments were not performed for specific temperatures, since (i) the temperature range of the measurements is small, (ii) adjustment was only carried out in this range, and (iii) the vibrating tube temperature has never been outside this range so far.

The temperature sensor inside the VTD was calibrated using thermistors, which were adjusted at PTB. For the measurements the thermistors were placed inside the vibrating tube, in which an aqueous liquid was filled. The temperature gradient along the tube to the connecting ports was also determined and considered in uncertainty. The standard uncertainty in temperature is 5 mK.

The manometer was calibrated at PTB. The zero-point drift was compensated for before each measurement series. To that end, the manometer was compared to the one used for density determination at atmospheric pressure. The zero-point drift during a measurement is negligible. The standard uncertainty of the pressure measurement is 1500 Pa.

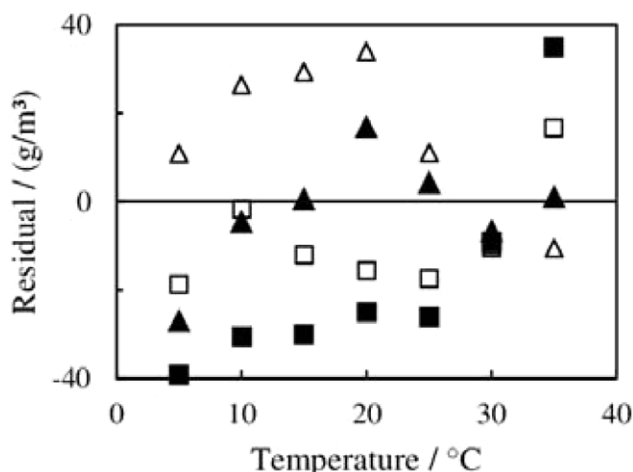
**3.1.6. Calculation.** The substitution values were calculated and the reference densities interpolated as described in section 2.1.6.

## 3.2. Results

**3.2.1. Adjustment.** For the new adjustment approach that is described in appendix B.2, knowledge of outer radius and wall thickness values as well as of the elastic modulus and Poisson's ratio of the vibrating tube is necessary. The values are given in table 3.

Densimeter adjustment was performed in two stages: firstly adjustment at atmospheric pressure was performed using a few liquids with well-known densities. *N*-nonane, water, and tetrachloroethylene were each measured in the temperature range of 5 °C to 35 °C. Their densities at 20 °C are about 720 kg m<sup>-3</sup>, 998 kg m<sup>-3</sup>, and 1622 kg m<sup>-3</sup>, respectively, to cover the entire seawater density range. Afterwards the coefficients of (B.12) to (B.14) were fitted to the following reference values: (i) *n*-nonane reference values were available from hydrostatic weighing with a standard uncertainty of 2.5 g m<sup>-3</sup>, (ii) water reference values were taken from Wagner and Pruß [17] with a standard uncertainty of 0.5 g m<sup>-3</sup> and corrected for isotopic composition, and (iii) tetrachloroethylene values were available with a standard uncertainty of 25 g m<sup>-3</sup> from measurements using a DMA 5000M. Figure 8 shows the residuals of this fit. The tetrachloroethylene residuals, which have the highest uncertainty, also have the highest residuals. The vibrating tube of the high pressure VTD is made of a pressure resistant alloy. The ratio of the mass of the liquid inside the tube to the mass of the tube material is therefore much lower compared to the ratio of the device for atmospheric pressure, which uses a glass tube. In consequence, the oscillation period is less sensitive to the liquid density. Also temperature hysteresis is not compensated for by a reference oscillator. This results in a significantly lower repeatability.

Secondly coefficients of (B.18) were fitted to measurements of water at high pressures using reference values from Wagner and Pruß [17]. Multiple runs were carried out using the same procedure to minimize deviations due to repeatability as shown in figure 9. The uncertainty of the water reference values for high pressure is ten times higher than for atmospheric pressure. The mean residuals can therefore be higher compared to atmospheric pressure. The standard deviation of



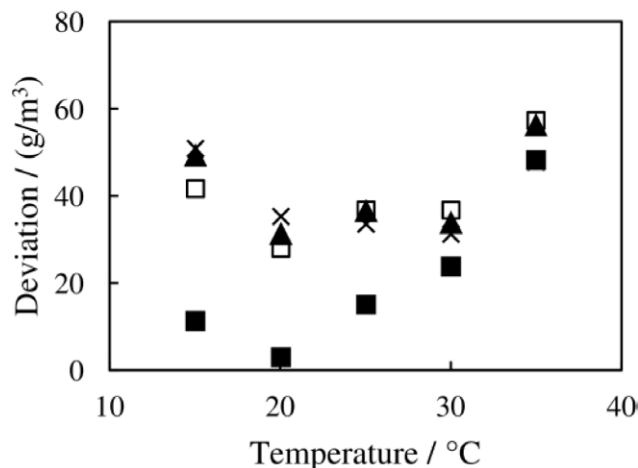
**Figure 9.** Some residuals of adjustment at high pressure using water. Pressure was increased at constant temperatures. Overall standard deviation is  $19 \text{ g m}^{-3}$ . ■ 1st run—0.3 MPa, □ 1st run—40 MPa, ▲ 2nd run—0.3 MPa, △ 2nd run—40 MPa.

the adjustment for high pressure is included in the uncertainty model for the substitution method, see appendix A.

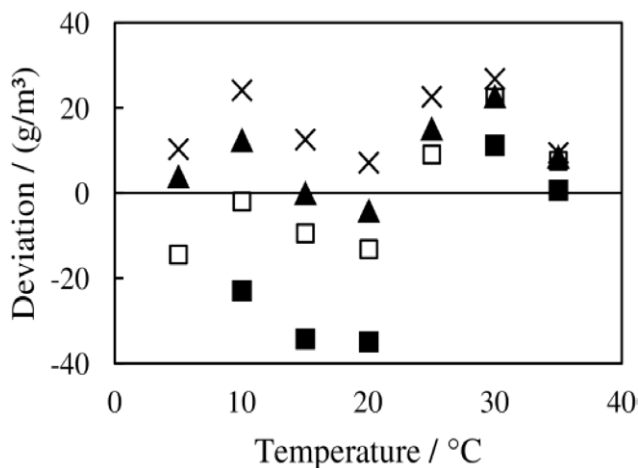
A validation of the adjustment for high pressures was not possible, since the uncertainty of reference data from literature is higher than that resulting from measurements using our adjustment approach. The adjustment was therefore only checked up to 30 MPa using *n*-nonane and 2,4-dichlorotoluene based on literature data of Schilling *et al* with a standard uncertainty of 0.01% [18], shown in figure 10. *N*-nonane was also used for adjustment at atmospheric pressure. The *n*-nonane literature data was scaled to the measured density at 20 °C and 0.1 MPa to minimize uncertainty influences caused by the delivered charge. Standard uncertainty of the scaling data was  $2.5 \text{ g m}^{-3}$ . The deviations are positive and systematically related to temperature. An analysis of the deviations was not conducted, since the standard uncertainty of the *n*-nonane literature values is  $70 \text{ g m}^{-3}$ .

2,4-dichlorotoluene was used to check the adjustment for linearity. The measurement values of the 2,4-dichlorotoluene, which were calculated using the resulting adjustment equation, were compared to the data of Schilling *et al* [18]. They developed an EOS based on their measurements using a single sinker densimeter. This EOS was scaled to the 2,4-dichlorotoluene density measured at PTB at 20 °C and 0.1 MPa with a standard uncertainty of  $25 \text{ g m}^{-3}$  to minimize density deviations caused by different charges. The 2,4-dichlorotoluene density is about  $1250 \text{ kg m}^{-3}$  at 20 °C and 0.1 MPa, and is thus within the densities of water ( $998 \text{ kg m}^{-3}$ ) and tetrachloroethylene ( $1622 \text{ kg m}^{-3}$ ), which were used for adjustment at atmospheric pressure. The deviations shown in figure 11 are smaller than the uncertainty. The linearity of the adjustment is consequently validated within the uncertainty of the literature values at a density significantly higher than that of seawater.

**3.2.2. Repeatability.** Multiple fillings of a filtered natural seawater sample were measured on various days. The results for 65 MPa scatter within a range of  $6 \text{ g m}^{-3}$ , see figure 12 (a). The standard deviation found from these measurements was



**Figure 10.** Deviation from literature values of *n*-nonane [18] at high pressures. Standard uncertainty of literature values is about  $70 \text{ g m}^{-3}$ . ■ 0.3 MPa, □ 10 MPa, ▲ 20 MPa, × 30 MPa.

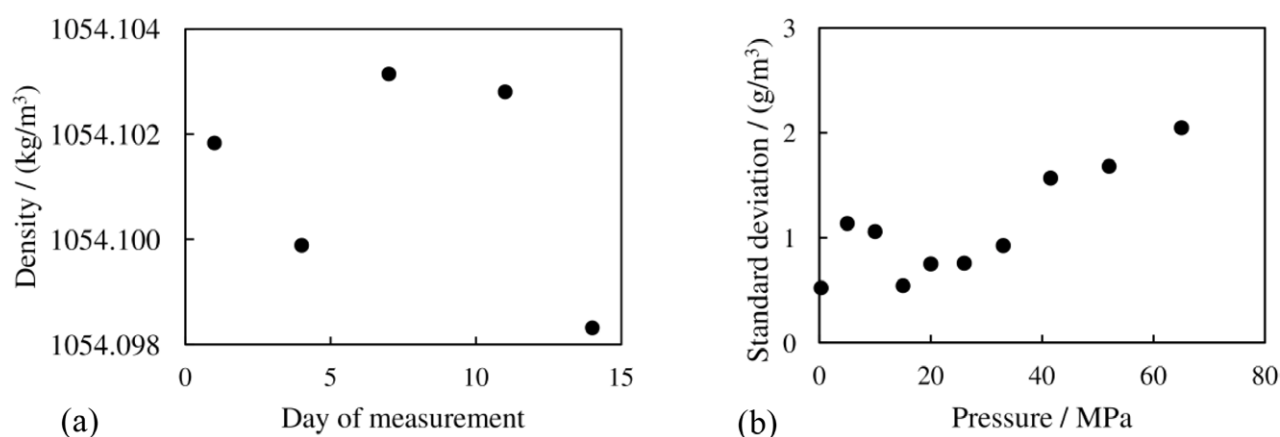


**Figure 11.** Deviation from literature values of 2,4-dichlorotoluene [18] at high pressures. Standard uncertainty of literature values is about  $120 \text{ g m}^{-3}$ . ■ 0.3 MPa, □ 10 MPa, ▲ 20 MPa, × 30 MPa.

also the highest compared to those for the lower pressures, see figure 12 (b). The standard deviation of the measurements for each pressure tends to increase with the pressure. A standard deviation of  $2.5 \text{ g m}^{-3}$  with four degrees of freedom for all pressures is used as the uncertainty contribution due to repeatability to calculate the uncertainty of the substitution method.

**3.2.3. Uncertainty.** Table 4 shows the uncertainty budget of a measurement of seawater with a practical salinity of 35 for 0.3 MPa, which is based on the uncertainty model given in appendix A. The uncertainties of water reference values, repeatability, and adjustment are the only significant contributions to measurement uncertainty. The contributions from temperature and pressure are insignificant. Standard uncertainty is  $7 \text{ g m}^{-3}$ .

Table 5 shows the uncertainty budget of a measurement of seawater with a salinity of 35 for 65 MPa, with uncertainties resulting from the determination of the vibrating tube properties being considered. Since the standard uncertainty of the water reference values is increased to  $15 \text{ g m}^{-3}$  for pressures



**Figure 12.** Repeated substitution measurements of filtered seawater with a salinity of 35 at 15 °C at high pressures. Results for 65 MPa (a) and standard deviations for all pressures (b).

**Table 4.** Uncertainty budget of a substitution measurement of seawater with a salinity of 35 for 0.3 MPa.

| Quantity                     | Unit               | Value              | Uncertainty               | Sensitivity <sup>b</sup> | $\nu$    | Significance |
|------------------------------|--------------------|--------------------|---------------------------|--------------------------|----------|--------------|
| Temperature—Measurement      | K                  | 288.15             | 0.005                     | $-6.87 \times 10^{-2}$   | $\infty$ | 0%           |
| Pressure—Measurement         | Pa                 | $0.3 \times 10^6$  | 1500                      | $2.31 \times 10^{-8}$    | $\infty$ | 0%           |
| Density—Reference—EOS        | kg m <sup>-3</sup> | 999.1953           | 0.005                     | 1                        | $\infty$ | 50%          |
| Repeatability                | kg m <sup>-3</sup> | —                  | 0.003                     | 1                        | 4        | 13%          |
| Adjustment                   | kg m <sup>-3</sup> | ref/s <sup>a</sup> | 0.019                     | ref/s <sup>a</sup>       | 99       | 37%          |
| Standard uncertainty         |                    |                    | 0.0071 kg m <sup>-3</sup> |                          |          |              |
| Effective degrees of freedom |                    |                    | 139                       |                          |          |              |

<sup>a</sup> Contribution from adjustment can be separated into contributions of the densities of pure water (ref) and seawater (s), but was summarized for clarity.

<sup>b</sup> Units are kg m<sup>-3</sup> / K, kg m<sup>-3</sup> / Pa, etc.

**Table 5.** Uncertainty budget of a substitution measurement of seawater with a salinity of 35 for 65 MPa.

| Quantity                     | Unit               | Value                 | Uncertainty               | Sensitivity             | $\nu$          | Significance |
|------------------------------|--------------------|-----------------------|---------------------------|-------------------------|----------------|--------------|
| Temperature—Measurement      | K                  | 288.15                | 0.005                     | $-4.48 \times 10^{-2}$  | $\infty$       | 0%           |
| Pressure—Measurement         | Pa                 | $65 \times 10^6$      | 1500                      | $-1.83 \times 10^{-8}$  | $\infty$       | 0%           |
| Density—Reference—EOS        | kg m <sup>-3</sup> | 1027.444              | 0.015                     | 1                       | $\infty$       | 82%          |
| Elastic modulus—Measurement  | Pa                 | $205 \times 10^9$     | $10 \times 10^9$          | $-3.93 \times 10^{-13}$ | 1 <sup>a</sup> | 6%           |
| Radius—Measurement           | M                  | $1.59 \times 10^{-3}$ | $0.01 \times 10^{-3}$     | $5.05 \times 10^1$      | 1 <sup>a</sup> | 0%           |
| Wall thickness—Measurement   | M                  | $0.30 \times 10^{-3}$ | $0.01 \times 10^{-3}$     | $-2.70 \times 10^2$     | 1 <sup>a</sup> | 3%           |
| Poisson's ratio—Measurement  | —                  | 0.307                 | 0.015                     | $-4.69 \times 10^{-2}$  | 1 <sup>a</sup> | 0%           |
| Repeatability                | kg m <sup>-3</sup> | —                     | 0.003                     | 1                       | 4              | 2%           |
| Adjustment                   | kg m <sup>-3</sup> | ref/s                 | 0.019                     | ref/s                   | 99             | 6%           |
| Standard uncertainty         |                    |                       | 0.0169 kg m <sup>-3</sup> |                         |                |              |
| Effective degrees of freedom |                    |                       | 247                       |                         |                |              |

<sup>a</sup> Values are estimated.

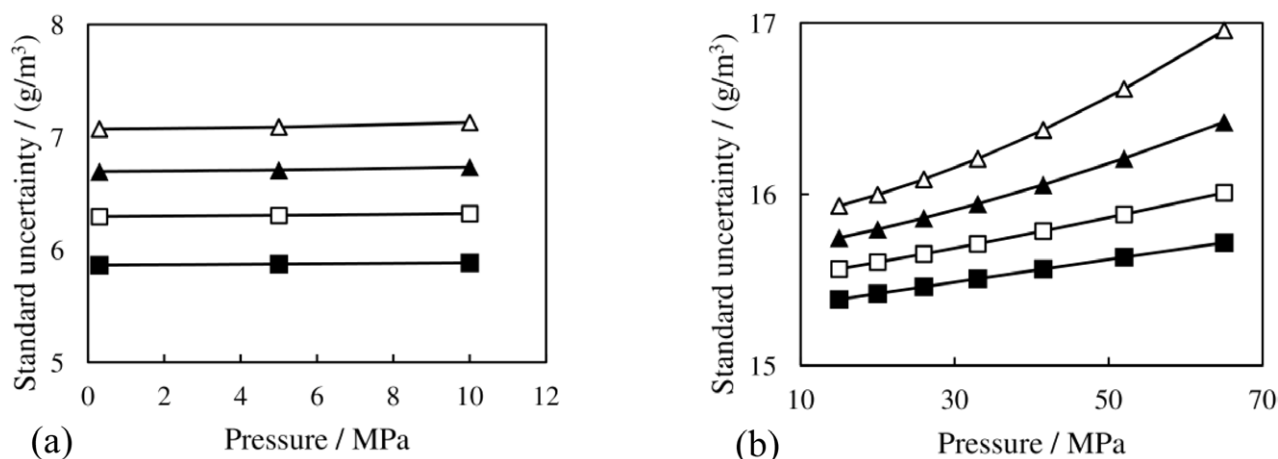
higher than 10 MPa, this uncertainty contributes 82% to the overall uncertainty. Less than 10% is contributed by the uncertainties of the vibrating tube properties. Standard uncertainty is 17 g m<sup>-3</sup>.

If the substitution measurement is carried out at a lower salinity, the uncertainty contribution from adjustment decreases, because the seawater density gets closer to the water density. The dependence of uncertainty on salinity and pressure is given in figure 13 (a) for pressures up to 10 MPa, at which the standard uncertainties of the reference values and repeatability are 5 g m<sup>-3</sup> and 2.5 g m<sup>-3</sup>, respectively, thereby dominating the budget. The dependence of uncertainty on salinity causes an increase of the standard uncertainty of up to 1 g m<sup>-3</sup>. The dependence on pressure can be neglected.

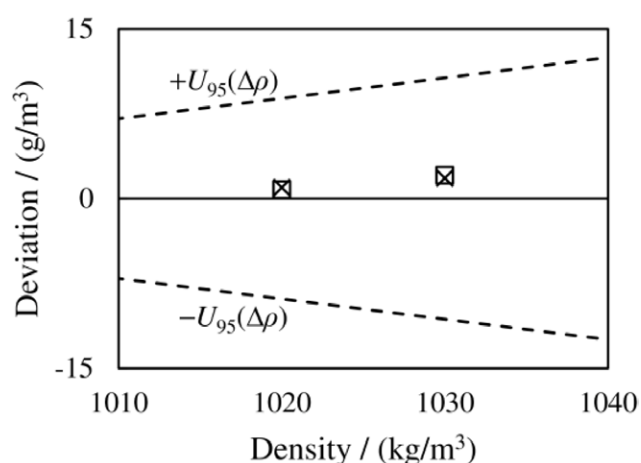
The uncertainty for pressures up to 65 MPa is given in figure 13 (b). There the standard uncertainty of the reference values is 15 g m<sup>-3</sup>. At higher salinities the dependence of uncertainty on pressure in the range of 10 MPa up to 65 MPa causes an increase of the standard uncertainty of up to 1 g m<sup>-3</sup>. At higher pressures the dependence on salinity causes an increase of up to 1.5 g m<sup>-3</sup>.

Since the dependence on temperature and vibrating tube properties is of minor significance in the temperature range of 5 °C to 35 °C, the uncertainty dependence on salinity shown in figure 13 may also be taken for these temperatures.

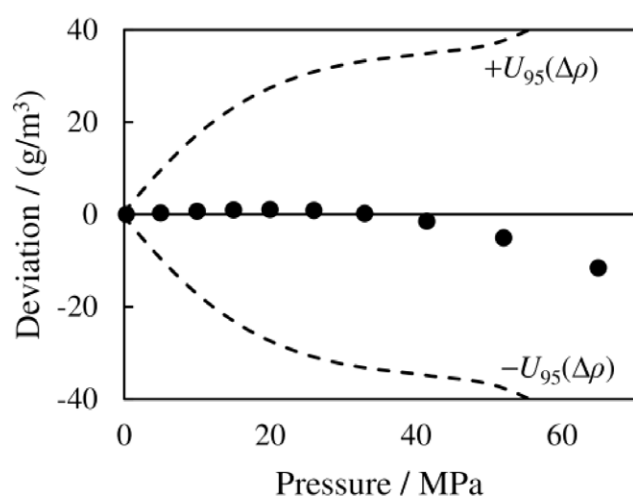
**3.2.4. Validation.** A linearity check of the high pressure densimeter DMA HP at atmospheric pressure using the



**Figure 13.** Dependence of uncertainty on salinity and pressure—up to 10 MPa (a) and to 65 MPa (b). ■ Salinity 5, □ 15, ▲ 25, △ 35.



**Figure 14.** Deviation of high pressure VTD from two atmospheric pressure VTDs (□ VTD 1 and × VTD 2) using the same premixed salt solutions and substitution method at 15 °C.  $U_{95}(\Delta\rho)$ —expanded uncertainty of deviations.



**Figure 15.** Deviation of high pressure substitution measurements of standard seawater with a salinity of 35 at 10 °C from calculated densities using compressibility data [19].  $U_{95}(\Delta\rho)$ —expanded uncertainty of deviations.

substitution method has been undertaken using liquids with well-known data. To this end, measurements of the same premixed aqueous sodium chloride solutions with target densities of  $1020 \text{ kg m}^{-3}$  and  $1030 \text{ kg m}^{-3}$  have been carried out using the high pressure densimeter and two DMA 5000M, given in figure 14. Both atmospheric densimeters were previously checked for linearity by comparison measurements with hydrostatic weighing apparatus. The deviations are well within the uncertainty of the deviations.

For high pressures there is no possibility to compare density measurements directly. Compressibility data of Bradshaw and Schleicher [19] were therefore compared to our measurements. Bradshaw and Schleicher measured the dependence of seawater compressibility on pressure at 10 °C and salinities around 35 using a dilatometer. Since they stated only uncertainties for their absolute volume measurements, we used their raw data of the measured volumes and recalculated the compressibility as a function of salinity and pressure, thereby treating the stated uncertainties like standard uncertainties. The resulting compressibility function was then used to compute high pressure densities relative to our substitution density at atmospheric pressure. To evaluate the deviation between the density derived from compressibility and our substitution density, the uncertainty of the density derived from compressibility was calculated using the Monte Carlo method. The resulting deviations and uncertainties are shown in figure 15. Up to 40 MPa the deviation is below  $2 \text{ g m}^{-3}$  and increases with higher pressures up to  $12 \text{ g m}^{-3}$ . The uncertainty is always significantly higher than the deviation. Our measurement results are hence consistent with the density data derived from the studies of Bradshaw and Schleicher.

#### 4. Conclusion

A substitution method using a vibrating tube densimeter and ultrapure water as a reference liquid was realized to carry out density measurements on seawater at atmospheric and high pressures. The expanded uncertainty for measurements at atmospheric pressure using this method was calculated to

be less than  $2\text{ g m}^{-3}$  for salinities up to 35 and temperatures from  $5\text{ }^{\circ}\text{C}$  to  $35\text{ }^{\circ}\text{C}$ . A validation of the realized method and the uncertainty calculations was undertaken by comparison measurements with hydrostatic weighing apparatus. The uncertainty calculations for measurements at high pressures yielded  $18\text{ g m}^{-3}$  for pressures up to 10 MPa and  $36\text{ g m}^{-3}$  for pressures up to 65 MPa. Literature data of seawater were compared to the measured substitution densities at  $10\text{ }^{\circ}\text{C}$  and yielded very good agreement within the stated uncertainty. The uncertainty models presented can be used for extending the uncertainty calculation to higher temperatures, salinities, and pressures.

The method presented will be used to establish a metrologically traceable relationship between density and salinity in a wide range of temperature and pressure to ensure consistency of oceanographic salinity measurements over long periods<sup>4</sup>.

## Acknowledgments

This work was funded by the European Metrology Research Programme, EMRP Project ENV05. The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union.

We appreciate the isotopic abundance measurements of oxygen-18 and hydrogen-2 in water performed by the *Helmholtz-Zentrum für Umweltformung* (UFZ) in the working group of Stephan Weise (former *Labor für Stabile Isotope*).

## Appendix A. Uncertainty model of the substitution measurements

### A.1. Derivation of the model equation

**A.1.1. Similarity of the reference in measurement and calculation** The uncertainty model of the substitution measurements is based on (A.1):

$$\rho_{\text{subs}} = \rho_{\text{ref}} - \rho_{\text{ref,mes}} + \rho_{\text{s,mes}} \quad (\text{A.1})$$

where  $\rho_{\text{subs}}$  is the unknown substitution density and  $\rho_{\text{s,mes}}$  is the measured density of the seawater sample, respectively, and  $\rho_{\text{ref}}$  is the well-known density and  $\rho_{\text{ref,mes}}$  is the measured density of the water reference, respectively.

The calculated reference density  $\rho_{\text{ref}}$  is used to represent the best estimate density of the water, which is measured in the densimeter. The state of this water may be different from the state, for which the reference density was calculated, thereby causing a deviation in the density difference  $\rho_{\text{ref}} - \rho_{\text{ref,mes}}$ .

One contribution to this deviation results from (i) a difference between the measurement temperature  $T$  and the temperature  $T^*$ , for which the reference density was calculated. The density effect of this difference can be described by  $\partial\rho_{\text{ref}}/\partial T \cdot (T - T^*)$  or  $\rho_{\text{ref}} \cdot \alpha_{\text{ref}} \cdot (T - T^*)$  where  $\alpha_{\text{ref}}$  is the coefficient of thermal expansion.

Another contribution results from (ii) a difference between the measurement pressure  $p$  and the pressure  $p^*$ , for which the reference density was calculated. The density effect of this difference can be described by  $\partial\rho_{\text{ref}}/\partial p \cdot (p - p^*)$  or  $\rho_{\text{ref}} \cdot \kappa_{\text{ref}} \cdot (p - p^*)$  where  $\kappa_{\text{ref}}$  is the coefficient of compressibility.

Analogous contributions result from (iii) a difference between the measurement relative aeration  $\varphi$  and the relative aeration  $\varphi^*$  used for calculation, (iv) a difference between the measurement isotopic abundance in deuterium  $\delta_{\text{D}}$  and  $\delta_{\text{D}}^*$ , and (v) a difference between measurement isotopic abundance in oxygen-18  $\delta_{18}$  and  $\delta_{18}^*$ .

The overall density deviation of the water reference in measurement and calculation resulting from the particular differences (i–v) mentioned above are summarized by:

$$\delta\rho_{\text{ref}} = \rho_{\text{ref}}(T, p, \varphi, \delta_{\text{D}}, \delta_{18}) - \rho_{\text{ref}}(T^*, p^*, \varphi^*, \delta_{\text{D}}^*, \delta_{18}^*) \quad (\text{A.2})$$

where  $\rho_{\text{ref}}(T, p, \varphi, \delta_{\text{D}}, \delta_{18})$  is the reference density in the state of measuring and  $\rho_{\text{ref}}(T^*, p^*, \varphi^*, \delta_{\text{D}}^*, \delta_{18}^*)$  is the reference density in the state of calculation.

The measurement temperature  $T$ , pressure  $p$ , etc. are used to estimate the reference density state of calculation, and hence used to calculate the reference density. The density deviation  $\delta\rho_{\text{ref}}$  is therefore caused by systematic uncertainties in these quantities. In the uncertainty model this is considered by calculating  $\rho_{\text{ref}}(T, p, \varphi, \delta_{\text{D}}, \delta_{18})$  with the assigned uncertainties  $u(T)$ ,  $u(p)$ , etc., but calculating  $\rho_{\text{ref}}(T^*, p^*, \varphi^*, \delta_{\text{D}}^*, \delta_{18}^*)$  without uncertainties and extending the model equation for uncertainty:

$$\rho_{\text{subs}} = \rho_{\text{ref}} - (\rho_{\text{ref,mes}} + \delta\rho_{\text{ref}}) + \rho_{\text{s,mes}} \quad (\text{A.3})$$

**A.1.2. Similarity of the sample in measurement and calculation** In the substitution measurements the difference between the calculated reference density and the measured reference density  $\rho_{\text{ref}} - \rho_{\text{ref,mes}}$  is used to correct the measured sample density  $\rho_{\text{s,mes}}$ . The calculation temperature and pressure are equal to the measurement temperature and pressure. The equation for calculation of the density difference is consequently valid for  $T^*$  and  $p^*$ .

The density deviation for the model equation, which is caused by differences from this temperature and pressure during the measurement of the seawater sample is expressed analogously to (A.2):

$$\delta\rho_{\text{s}} = \rho_{\text{s}}(T, p) - \rho_{\text{s}}(T^*, p^*) \quad (\text{A.4})$$

where  $\rho_{\text{s}}(T, p)$  is the sample density calculated with the assigned uncertainties  $u(T)$  and  $u(p)$ , and  $\rho_{\text{s}}(T^*, p^*)$  is calculated without uncertainties.

Other uncertainties in, for example, aeration, salinity, isotopic composition, etc. of the seawater sample are not considered, since they are not used to determine the unknown substitution density.

The seawater density  $\rho_{\text{s}}$  for determination of  $\delta\rho_{\text{s}}$  in the uncertainty model is calculated using the EOS given by Feistel [20] that was adopted by the Intergovernmental Oceanographic Commission in 2009 as the Thermodynamic

<sup>4</sup> The data of seawater density gained by this method in the salinity-, temperature-, and pressure ranges mentioned above are planned to be published in *Ocean Science*.

Equation of Seawater 2010 (TEOS-10). The uncertainty in salinity, which is necessary to calculate  $\rho_s$  using TEOS-10, or uncertainties in other quantities, which may affect the calculation of  $\rho_s$  to determine  $\delta\rho_s$ , are considered to be negligible for this purpose.

(A.3) is extended to yield the final model equation of the substitution measurements:

$$\rho_{\text{subs}} = \rho_{\text{ref}} - (\rho_{\text{ref,mes}} + \delta\rho_{\text{ref}}) + \rho_{\text{s,mes}} + \delta\rho_s \quad (\text{A.5})$$

#### A.2. Reference density $\rho_{\text{ref}}$

The reference densities of pure water  $\rho_{\text{ref}}$  were determined using reference equations of state. Harvey *et al* [21] discussed the usage of two major reference EOS for water. The first EOS was given by Tanaka *et al* [22] and was adopted by the International Committee for Weights and Measures (CIPM). This EOS is valid for fully degassed water with Vienna Standard Mean Ocean Water (VSMOW) isotopic composition in the temperature range 0 °C to 40 °C at atmospheric pressure. Corrections for isotopic composition and aeration are stated. The second EOS for a wider range of temperature and pressure was given by Wagner and Pruß [17] and was adopted by the International Association of the Properties of Water and Steam in 1995 (IAPWS-95). This EOS is also valid for degassed water of VSMOW composition. Harvey *et al* recommended using the EOS of Tanaka *et al* for atmospheric pressure, if the temperature range of interest is between 1 °C and 40 °C, and using the IAPWS-95 formulation for larger temperature ranges and higher pressures. Since our measurements are planned to include high pressure measurements, the IAPWS-95 formulation was used to calculate the reference densities of water for all measurements. To this end, the correction for isotopic composition as suggested by Tanaka *et al* was transferred analogously to densities calculated using IAPWS-95. The correction for aeration of Harvey *et al* [12] was used following the recommendations of Harvey *et al* [21]. The equation of water density for uncertainty modelling is:

$$\rho_{\text{ref}} = \rho_0(T^*, p^*) \cdot \Gamma\rho_0 \quad (\text{A.8})$$

where  $\rho_0$  is the water density as given by Wagner and Pruß [17] and  $\Gamma\rho_0$  is the term for the correction of isotopic composition and aeration that is described by:

$$\Gamma\rho_0 = 1 + \frac{\Delta\rho_{\text{cp}}(\delta_D^*, \delta_{18}^*)}{\rho_0(3.98\text{ °C}, 101325\text{ Pa})} + \frac{\Delta\rho_{\text{air}}(T^*, \varphi^*)}{\rho_0(T^*, 101325\text{ Pa})} \quad (\text{A.9})$$

where  $\Delta\rho_{\text{cp}} = 0.233\text{ kg m}^{-3} \cdot \delta_D^* + 0.0166\text{ kg m}^{-3} \cdot \delta_{18}^*$  and  $\Delta\rho_{\text{air}}(T^*, \varphi^*)$  are the corrections for isotopic composition and aeration given by Tanaka *et al* [22] and Harvey *et al* [21].

$\delta_D^*$  is the amount of substance ratio  $[D]/[H]$  and  $\delta_{18}^*$  is the amount of substance ratio  $[^{18}\text{O}]/[^{16}\text{O}]$  relative to VSMOW composition, respectively, thus  $\delta_D = ([D]/[H])/([D]/[H])_{\text{VSMOW}} - 1$  and  $\delta_{18} = ([^{18}\text{O}]/[^{16}\text{O}])/([^{18}\text{O}]/[^{16}\text{O}])_{\text{VSMOW}} - 1$ .  $\delta_D$  and  $\delta_{18}$  of tap water from Braunschweig, Germany, which was used for the substitution measurements, were measured by the UFZ. They are  $-0.0085$  with a standard uncertainty of  $3 \times 10^{-5}$  and  $-0.059$  with a standard uncertainty of  $4 \times 10^{-4}$ , respectively.

Standard uncertainty of the water reference density  $\rho_0$  stated by Wagner and Pruß [17] is  $0.5 \times 10^{-6}$  at atmospheric pressure,  $5 \times 10^{-6}$  up to 10 MPa, and  $15 \times 10^{-6}$  to 100 MPa.

#### A.3. Measured densities $\rho_{\text{ref,mes}}$ and $\rho_{\text{s,mes}}$

If a substitution measurement is performed, there is a contribution to uncertainty from the densimeter adjustment. This uncertainty increases with the difference of seawater density and water density.

For atmospheric pressure limited information on factory adjustment is available. The contribution from adjustment was therefore estimated assuming that (i) the measurement uncertainties of the pure water and seawater density values are equal, thus  $u(\rho_{\text{ref,mes}}) = u(\rho_{\text{s,mes}})$ , and (ii) since these measurements are carried out using the same instrument at nearly identical conditions the correlation coefficient is close to 1; we used  $r_{\text{ref,s}} = \rho_{\text{ref,mes}}/\rho_{\text{s,mes}}$ .

For high pressure the adjustment was undertaken using water, which is also used as a reference liquid for the substitution. The uncertainty contribution from adjustment was estimated assuming that (i) the standard uncertainties of the pure water and seawater densities measured are equal to the standard deviation of the adjustment equation fitted to the high pressure densities of water, thus  $u(\rho_{\text{ref,mes}}) = u(\rho_{\text{s,mes}}) = \sigma$ , and (ii) the correlation coefficient is equal to that at atmospheric pressure.

#### A.4. Random uncertainty contributions

Random uncertainty contributions of the input quantities and their effects on the measured data were estimated from repeated measurements. Since measurements are very time consuming, the number of measurements to estimate repeatability was low. The coverage factor was therefore calculated using the effective degrees of freedom. To this end, the Guide to the Expression of Uncertainty in Measurement (GUM) [23] recommends the Welch-Satterthwaite equation. Since this equation does not include correlations, further approaches were presented by other authors, for example, by Kessel and Kacker [24] and Castrup [25]. The latter was used to calculate the coverage factor for the overall uncertainty.

## Appendix B. Adjustment of the high pressure densimeter

#### B.1. Summary of existing approaches

Vibrating tube densimeters have to be adjusted using reference fluids. Since the number of reference liquids for high pressures with an uncertainty significantly less than  $100\text{ g m}^{-3}$  is small, many approaches to minimize the number of liquids needed for adjustment were developed. Water reference density values used at high pressures have an uncertainty of  $10\text{ g m}^{-3}$  up to 10 MPa and  $30\text{ g m}^{-3}$  to 100 MPa [17]. Uncertainties of other reference liquids in the range of  $700\text{ g m}^{-3}$  to  $1300\text{ g m}^{-3}$  are usually higher than  $100\text{ g m}^{-3}$ .

Uncertainties of liquids with higher densities are again higher. Therefore, a risk of nonlinearity of existing adjustment procedures is given, which can increase the uncertainty of a substitution measurement aiming at an uncertainty of  $20 \text{ g m}^{-3}$  to  $40 \text{ g m}^{-3}$ . For this purpose, adjustment approaches were screened for the specific modelling and its advantages with the aim to develop a new approach. Requirements on the new approach were to use only one reference liquid for adjustment at high pressures and to minimize linearity effects, which are related to modelling.

One possible equation results from a model of an open-ended hollow cylinder, of which one end is clamped in a block, whose counter mass is infinite. From this model, the following equation can be derived:

$$\rho = A_0 + A_2 \cdot \tau^2 \quad (\text{B.1})$$

where  $\tau$  is the harmonic oscillation period of the vibrating tube, and  $A_0$  is a coefficient that is proportional to the quotient of the mass  $m_U$  and the inner volume  $V_U$  of the empty vibrating tube:

$$A_0 \propto \frac{m_U}{V_U} \quad (\text{B.2})$$

$A_2$  considers the mechanical properties, for example, stiffness. It is proportional to the quotient of a mechanical coupling constant  $K$  and the inner volume  $V_U$  of the tube:

$$A_2 \propto \frac{K}{V_U} \quad (\text{B.3})$$

Since the inner volume and the mechanical coupling constant depend on temperature and pressure, the coefficients  $A_0$  and  $A_2$  also depend on temperature and pressure, and it consequently makes sense to use two reference liquids for adjustment. Since there are only few reference liquids, more detailed modelling approaches of the vibrating tube were developed. In 1989, Niesen [26] developed a model, in which  $A_0 = f(T, p)$  and  $A_2 = f(T)$ . It was thus possible to use only one reference fluid for high pressures, and either two reference fluids for atmospheric pressure or a vacuum and one reference fluid. Niesen [26] determined the coefficients using a vacuum and either nitrogen or water depending on pressure. In 1992, Lagourette *et al* [27] analysed whether it is more accurate to assume either  $A_0$  or  $A_2$  as pressure independent. They came to the conclusion that the approach of Niesen [26] is more suitable, whereby only  $A_0$  is pressure dependent. In 1998, Holcomb and Outcalt [28] derived an adjustment equation that is based on physical modelling similar to that of Niesen [26]. In 2008, Comunas *et al* [29] modified the approach of Lagourette *et al* [27] for adjustments at temperatures higher than  $100^\circ\text{C}$  at atmospheric pressure. This was adopted, for example, by Segovia *et al* [30] in 2009.

As far back as 1994, Stabinger [31] discussed major sources that cause nonlinearity in the density of a VTD for measurements at atmospheric pressure. These were (i) an uneven mass distribution along the vibrating tube due to mountings, fluid density, and the shape of the tube, (ii) the finite counter mass that causes the system to be a coupled oscillation system, and

(iii) parasitic resonant effects due to the housing of the measuring cell. Stabinger recommended using a third reference liquid and an additional mathematical correction for equations like (B.1) to achieve an uncertainty of  $0.02 \text{ kg m}^{-3}$ .

From 2001 until 2014, Bouchot and Richon [32], Sanmamed *et al* [33], Lampreia *et al* [34], and May *et al* [35] each used an equation with a structure similar to (B.1), both adjustment coefficients being pressure dependent. Bouchot and Richon determined the parameters using physical modelling, one reference fluid for high pressures, and a vacuum. Sanmamed *et al* used physical modelling, two reference fluids for atmospheric pressure, and one for high pressures. Lampreia *et al* determined the coefficients using one reference fluid at high pressures and a vacuum, since they assumed the mechanical coupling constant  $K$  to be independent of pressure. May *et al* used physical modelling and recommended vacuum and one or two reference fluids at high pressures.

Anton Paar, the manufacturer of the DMA HP used for the density measurement at high pressures, recommends an adjustment equation of the following structure and determination of coefficients using reference fluids [36]:

$$\rho = A_0(T, p) + A_2(T, p) \cdot \tau^2 + A_4 \cdot \tau^4 \quad (\text{B.4})$$

where  $A_0$  and  $A_2$  are polynomial functions of temperature and pressure, and  $A_4$  is constant. The equation is recommended for use over wide ranges of density and indicates that model assumptions entering in (B.1) may differ significantly from the real system and cause nonlinearity.

Differences between the modelled systems and a real VTD system are: (i) Vibrating tubes have a shape for example, like a U or a Y. These are usually idealized as a straight uniform cylinder. (ii) To generate the vibration, additional masses are mounted on the vibrating tube. The shape of the vibrating tube and the mounted parts cause an oddly distributed mass. This is neglected in models that are based on an idealization of the vibrating tube of a uniform cross section. Furthermore, mass distribution depends on the density of the unknown fluid. (iii) The vibrating tube is clamped in a metallic block. This is neglected in models where the counter-mass of the mounting is assumed to be infinite. (iv) The diameter of the tube under pressure is increased. The axial length is decreased due to widening and is increased due to pressure-induced stress exerted on the axial directions of the ends. The latter is neglected in models that are based on an idealization with open-ended tubes.

## B.2. Derivation of the new approach

The new approach is based on (B.4), since the structure is similar to that of the adjustment equation of the more accurate VTD used for atmospheric pressure, whose vibrating tube has a similar geometry. Nonetheless, the coefficients were not determined by the use of reference liquids over the entire temperature and pressure range. Instead, a modelling approach was developed to enable adjustment at high pressures using only one reference liquid.

Holcomb and Outcalt [28] modelled the vibrating tube as a straight rod. Their modelling resulted in the following equations for  $A_0$  and  $A_2$ :

$$A_0 = -\frac{m_U}{V} \quad (\text{B.5})$$

$$A_2 = B = \frac{m_U}{V} \cdot \frac{L^3}{L_0^3} \cdot \frac{E}{E_0} \cdot \frac{I}{I_0} \cdot \omega_0^2 \quad (\text{B.6})$$

where  $m_U$  is the mass of the empty U-shaped tube,  $V$  the inner volume that is filled with the fluid to be measured,  $L$  the length of the rod,  $E$  the elastic modulus (Young's modulus),  $I$  is the second moment of inertia, and  $\omega$  the resonant frequency. 0 indicates the reference state that the variables refer to, for example, 293.15 K and 0.1 MPa.

Using (B.5) and (B.6) the parameters of (B.4) can be expressed as follows:

$$A_0 = 1/V(T, p) \cdot \text{const.} \quad (\text{B.7})$$

$$A_2 = f(T, p) \quad (\text{B.8})$$

$$A_4 = \text{const.} \quad (\text{B.9})$$

It is hence possible to determine the parameters at a reference state, say reference pressure, and refer to it at other states, say high pressure. That means that it is possible to adjust the parameters at atmospheric pressure with high accuracy and describe their change with increasing pressure by physical modelling and well-known reference fluids like water:

$$A_0 = \left( \frac{A_0(T, p)}{A_0(T, p_0)} \right) \cdot A_0(T, p_0) = \delta A_{00} \cdot A_{00} \quad (\text{B.10})$$

$$A_2 = \left( \frac{A_2(T, p)}{A_2(T, p_0)} \right) \cdot A_2(T, p_0) = \delta A_{20} \cdot A_{20} \quad (\text{B.11})$$

$$A_4 = A_4(T, p) \approx A_4(T, p_0) \approx a_{40} = \text{const.} \quad (\text{B.12})$$

$A_{00}$  and  $A_{20}$  describe the dependence on temperature at a reference pressure, for example, 0.1 MPa. They are determined by adjustment at atmospheric pressure using reference fluids with low uncertainty.  $\delta A_{00}$  and  $\delta A_{20}$  describe the change of the particular coefficient due to pressure relative to the reference pressure.  $\delta A_{00}$  is determined by physical modelling.  $\delta A_{20}$  is determined by adjustment at high pressures using water.  $A_{00}$  and  $A_{20}$  can be described using polynomial equations:

$$A_{00} = a_{00} + a_{01} \cdot T + a_{02} \cdot T^2 \quad (\text{B.13})$$

$$A_{20} = a_{20} + a_{21} \cdot T + a_{22} \cdot T^2 \quad (\text{B.14})$$

The inner volume  $V$  of the vibrating tube is modelled as a hollow cylinder with the length  $L$  and the inner radius  $r$ .  $\delta A_{00}$  is consequently expressed by:

$$\delta A_{00} = \left( \frac{V(T, p)}{V(T, p_0)} \right)^{-1} = \left( \frac{L(T, p)}{L(T, p_0)} \right)^{-1} \cdot \left( \frac{r(T, p)}{r(T, p_0)} \right)^{-2} = \delta L_0^{-1} \cdot \delta r_0^{-2} \quad (\text{B.15})$$

$\delta L_0$  and  $\delta r_0$  are derived from Lamé's equations [37] for a closed end, thick-walled hollow cylinder with an internal pressure  $p - p_0$  being applied, as for example described by Hearn [38]:

$$\delta L_0 \approx \frac{L(T_0, p)}{L(T_0, p_0)} \approx 1 + (p - p_0) \cdot \frac{r_0^2}{E} \cdot \frac{1 - 2 \cdot \nu}{R_0^2 - r_0^2} \quad (\text{B.16})$$

$$\delta r_0 \approx \frac{r(T_0, p)}{r(T_0, p_0)} \approx 1 + (p - p_0) \cdot \frac{(1 + \nu) \cdot R_0^2 + (1 - 2 \cdot \nu) \cdot r_0^2}{E \cdot (R_0^2 - r_0^2)} \quad (\text{B.17})$$

where  $r_0$  and  $R_0$  are the inner and outer radius of the tube at the reference state,  $\nu$  is Poisson's ratio, and  $E$  is the elastic modulus. Material data and information on the tube cross-sectional geometry are required to determine the geometry ratios. Knowing the tube length is not necessary.

$\delta A_{20}$  is described by a polynomial. Since it is determined from adjustment at high pressures relative to the reference pressure, its value is necessarily 1 at the reference pressure, thereby ensuring the adjustment of  $A_{00}$ ,  $A_{20}$ , and  $a_{40}$ .

$$\delta A_{20} = 1 + a_{201} \cdot \Delta p + a_{202} \cdot \Delta p^2 + a_{203} \cdot \Delta p^3 + a_{211} \cdot \Delta p \cdot T + a_{212} \cdot \Delta p \cdot T^2 \quad (\text{B.18})$$

where  $\Delta p = p - p_0$ . An advantage of this new approach is only one density standard being necessary for high pressures. Another advantage is the improvement of linearity in density, since more than one accurate density standard at atmospheric pressure can be used, and high pressure adjustment is relative to atmospheric pressure. An advantage in modelling is coefficient  $A_0$  being simple to describe and that there are no significant simplifications in the model assumptions. A disadvantage is uncertainty due to adjustment being increased with pressure and with density deviation of the unknown sample relative to the reference standard at high pressures.

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