

Response to RC3 (25 Sep 2017)

General comments

Thanks for the comments and questions, whose clarification contributes to the improvement of our article.

Specific comments

What is the impact of a zero-drift on the accuracy of a substitution measurement on standard seawater using a water reference? (Question 1)

The impact is negligible, provided that the densimeter is regularly quick-adjusted by the user (as it is usual in a well-managed lab).

A maximum deviation in air density of 20 g m^{-3} (reference minus measured) without a deviation in water density causes a non-considered deviation in the substitution density of seawater with salinity 35 of 0.5 g m^{-3} . If, additionally, there is a deviation in water density of -10 g m^{-3} (in the opposite direction), then a non-considered deviation in the substitution density of 0.8 g m^{-3} results.

However, we never saw such deviations during our substitution measurements. Additionally, such deviations are random, and are therefore considered in the repeatability of a substitution measurement, which for our measurements at atmospheric pressure was 1 g m^{-3} .

How is a DMA 5000 M densimeter adjusted?

The DMA (= density measurement apparatus) is adjusted by the manufacturer. The standards used for this purpose are multiple reference fluids (including air and water), whereof the density and viscosity are known, respectively. A quick-adjustment is provided to the customer using air and water. We performed a quick-adjustment before any substitution measurement.

Which formula is used to calculate the air density by the DMA 5000 M?

For the calculation of air density, the formula given by Spieweck and Bettin¹ for a relative humidity of 50 % is used by the internal firmware of the device². The air pressure is either measured by an internal barometer or provided by the customer. We used an external high precision barometer that was calibrated to provide the air pressure. Note that the DMA 5000 M manual² also contains data tables.

What is the density difference between this formula and the recent reference formula?

The formula given by Spieweck and Bettin¹ deviates significantly less than 1 g m^{-3} for 20°C and 50 %rh from the recent formulation of air density CIPM-2007³. A change in relative humidity of 10 % at 20°C changes the air density by 1 g m^{-3} . A deviation in the air density of 1 g m^{-3} yields the deviation in the seawater (substitution) density of 0.025 g m^{-3} that is insignificant in terms of uncertainty. We therefore decided to use the internal firmware calculation.

¹ Spieweck, F. and Bettin, H.: Review – Solid and liquid density determination, *Technisches Messen* 7/8, 1992, p. 291.

² Anton Paar GmbH: Manual – DMA 4100, DMA 4500 M, DMA 5000 M, Firmware-Version: V2.20, 18th January 2012.

A more recent manual (in English) may be obtained using the link (after registration):

<https://www.anton-paar.com/?elD=documentsDownload&document=5471&L=1>

³ Picard, A., Davis, R. S., Gläser, M. and Fujii, K.: Revised formula for the density of moist air (CIPM-2007), *Metrologia*, 45, 149–155, doi:10.1088/0026-1394/45/2/004, 2007.

How can the impact be estimated?

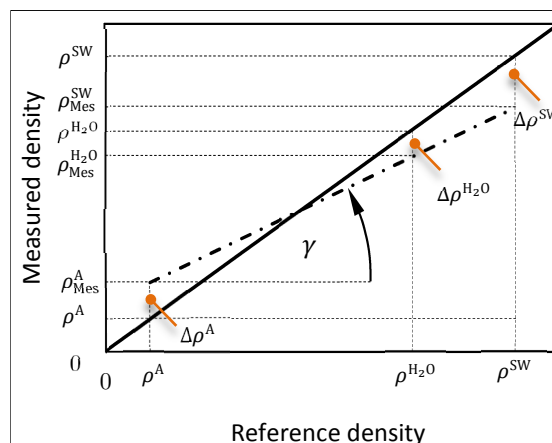
The impact can be estimated using the formula:

$$\Delta\rho_{SW} = (1 - \gamma) \cdot \Delta\rho_A + \gamma \cdot \Delta\rho_{H_2O} \text{ with } \gamma = (\rho_{SW} - \rho_A) / (\rho_{H_2O} - \rho_A),$$

where ρ_A and $\Delta\rho_A$ are the air reference density and deviation therefrom (ref. minus meas.), ρ_{H_2O} and $\Delta\rho_{H_2O}$ are the water reference density and deviation therefrom (ref. minus meas.), and $\Delta\rho_{SW}$ is the difference between substitution and measured seawater density (subs. minus meas.).

The idea behind the formula is illustrated in (and may be derived from) the figure below.

Figure. Linear characteristic curve of an ideal densimeter (—) and of a densimeter with a zero-offset (— · —).



Are there details on the substitution method yet not provided?

The substitution method does not correct a nonlinear characteristic curve (compare the linear characteristic curve in the figure above). Since the linearity of the DMA 5000 M and HP was checked before, please provide a hint to the reference. (Hint 2.1)

The following change was made to the manuscript at Page 3 Line 28 (from left to right):

2.1 Substitution method

[..] The uncertainty of a corrected seawater density resulting from a substitution measurement mainly depends on the uncertainty of the water reference, but also on the similarity of seawater and water in terms of their relevant thermophysical properties, as well as on the stability and linear characteristics of the densimeter used.

2.2 Materials

[..]

2.1 Substitution method

[..] The uncertainty of a corrected seawater density resulting from a substitution measurement mainly depends on the uncertainty of the water reference, but also on the similarity of seawater and water in terms of their relevant thermophysical properties, as well as on the stability and linear characteristics of the densimeter used. Note that the linearity is regularly checked in measurements on reference liquids with densities between 700 kg m^{-3} and 1600 kg m^{-3} ; furthermore, the linearity was particularly validated in the seawater density range by means of comparison measurements against a hydrostatic weighing apparatus for both the densimeters used for atmospheric and high pressure; details have been given by Schmidt et al. (2016).

2.2 Materials

[..]

Uncertainty at high pressure (Q. 2.2)

Reviewer: 'In this publication, their standard uncertainty is given to be 25 g m^{-3} and you give a standard uncertainty adjustment of 19 g m^{-3} at 65 MPa. In this case, how can you ensure an uncertainty of 0.008 (including the linearity in the budget) in salinity at high pressure and the deviations you give in Figure 12?

Authors: We are not quite sure what exactly is being asked. Therefore, we try to give step-by-step feedback.

Reviewer: 'At high pressure, the linearity was checked and corrected with 4 substances, the less precise having the higher densities.'

Authors: Certainly our publication describing the development and validation of the substitution densimeter⁴ is referred to.

Linearity check. In order to check the linearity of the substitution densimeter for high pressure, we performed comparison measurements against our substitution densimeter for atmospheric pressure that had been checked against a hydrostatic weighing densimeter before. To this end, we had premixed salt solutions and measured samples therefrom in each apparatus. Thus, the weighing densimeter served as reference to the atmospheric-pressure densimeter that again served as reference to the high-pressure densimeter. This linearity checks were performed at atmospheric pressure. The agreement between all those comparison measurements was better than $\pm 2 \text{ g m}^{-3}$, even for the high pressure densimeter.

Adjustment. The adjustment of the high-pressure densimeter is performed in two stages.

In the first stage the densimeter is adjusted for atmospheric pressure. Here, three liquids were used: *n*-nonane, water and tetrachloroethylene, each having densities at 20 °C of 720 kg m^{-3} , 998 kg m^{-3} , and 1622 kg m^{-3} . The standard uncertainty in tetrachloroethylene reference densities was 25 g m^{-3} .

In the second stage the densimeter is adjusted for high pressure. Here, only water was used.

Reviewer: 'In this publication, their standard uncertainty is given to be 25 g m^{-3} [...]'

Authors: Do you mean the uncertainty in the tetrachloroethylene reference densities used in adjustment for atmospheric pressure?

Reviewer: '[...]' and you give a standard uncertainty in adjustment of 19 g m^{-3} at 65 MPa.'

Authors: Certainly the uncertainty budget for a substitution measurement of seawater at 65 MPa is referred to, i.e. Table 5⁴. This budget is based on the uncertainty model described in Appendix A⁴. The standard uncertainty in adjustment of 19 g m^{-3} that is given in this table can only be used, if the correlation between the water and seawater density in the substitution measurement is taken into account.

Reviewer: 'In this case, how can you ensure an uncertainty of 0.008 (including the linearity in the budget) in salinity at high pressure [...]'

Authors: The uncertainty in salinity of 0.008 corresponds to the uncertainty in relative density, i.e. relative to water, of 6 g m^{-3} . This uncertainty results from the uncertainty budget (of Table 5⁴), which describes the uncertainty in absolute density, if the uncertainty of the water reference density is taken out.

Reviewer: '[...]' and the deviations you give in Figure 12?'

Authors: The deviation in Figure 12 has to be evaluated against its uncertainty. The deviation is within the uncertainty, thus there is consistency for high pressure.

⁴ Schmidt, H., Wolf, H. and Hassel, E.: A method to measure the density accurately to the level of 10^{-6} , Metrologia, 53, 2, 770–86, doi:10.1088/0026-1394/53/2/770, 2016.

Are there details on the substitution densimeter yet not provided?

What is the impact of the in/output assembly on the substitution density measured?

Measuring the density not using the substitution method: after a quick-adjustment, we never observed deviations $> \pm 5 \text{ g m}^{-3}$, even if the densimeter was filled manually using syringes that were directly and coarsely connected to the inlet of the oscillating U-tube. The inlet may be mechanically decoupled to avoid such deviations.

Measuring the density using the substitution method (and a permanent filling installation): such effects are eliminated, as the impact on the measurement of water and seawater density is identical and no parts are being moved during the measurements.

The density is determined from the oscillation frequency and has to be corrected for damping effects that are caused by the friction between fluid layers due to viscosity. To correct for this effect, the first harmonic oscillation frequency is used by the firmware⁵. The impact of the in/output assembly on density measurement therefore has to be considered before this background. Frankly speaking, the damping-corrected density has to be used instead of the non-damping-corrected density. Using the non-damping-corrected density in a substitution measurement of seawater can, based on our experience, cause the density being measured too high by up to 10 g m^{-3} , as any damping effects force the base frequency being too low, thereby pretending a higher density.

The DMAs inclination affects the measurement density by 2 g m^{-3} per 1° (degree). How was this considered? (Q. 3.2)

The effect is well-known, we measured exactly 1.82 g m^{-3} per 1° . The correction is multiplicative as gravitational forces are working only partly, if the inclination is not perpendicular to the direction of the gravitational force. The effect is therefore eliminated by an adjustment at the same inclination.

Apart from the fact that our DMAs are set up on fixed straight surfaces, such deviations are corrected by the substitution method. If a DMA is used without the substitution method, it can also be quick-adjusted (with air and water) at an inclination and then used afterwards. The decisive factor is that the inclination does not change between adjustment and measurement. This may be a problem in measurements aboard a ship.

How do you ensure that the tube is sufficiently long to avoid diffusion of the oil into the U-tube of the DMA HP during measurements at high pressure? (Q. 3.3)

The oil and water are not miscible, so there is always a phase boundary between both liquids. The phase boundary is reinforced, as the capillary tube in that both liquids meet has a small diameter of 1.6 mm. The density of the oil is lower than that of the water. We took advantage of that and installed the density measurement part at a lower level than the pressurization part that is filled with oil, thereby preventing convection downwards (into the DMA).

In addition, the filling line was rinsed with ethanol and water after each substitution measurement, thereby removing any oil that may stick to and creep on the inner tube wall, as such oil remains can disturb a clean replacement of seawater by water and vice versa. If, nonetheless, there is such a disturbance, this is seen in an increase in the water density measured or decrease in the seawater density measured, provided a measurement series (water – seawater – water – seawater – ... – water) is conducted. For the high pressure measurements, we performed usually 5 repeated substitution measurements per temperature-pressure density point, i.e. 11 liquid

⁵ Stabinger, H.: Density measurement using modern oscillating transducers, South Yorkshire Trading Unit, Sheffield, 1994.

replacements (water was always first and last); following the cleaning routine an impure replacement of liquids never occurred.

Page 9 Line 15: Replace 'to store the of seawater' by 'to store the seawater'. (H. 4)

The following change was made to the manuscript (from left to right):

The borosilicate vessels used to store the of seawater samples [..]	The borosilicate vessels used to store the seawater samples [..]
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Why do we speak of a linear dependence (on salinity) of the deviations of the Millero et al.-measurements from the density–salinity relation, when the deviations (shown in Fig. 11b) may suggest another type of dependence, too, e.g. a quadratic? (Q. 5)

The linear dependence (on salinity) of the density deviation between TEOS-10 and the density–salinity relation is obvious. To develop TEOS-10 in this salinity-temperature region (at atmospheric pressure) a combined dataset⁶ that consists of density data of Millero et al.⁷ and Poisson et al.⁸ was used^{9,10}. However, for combining, both the data were adjusted. In Fig. 11b (of the discussion paper) the adjusted data is shown.

In order to manifest the linear dependence, we should perhaps use the original magnetic float data of Millero et al.⁷ that was converted to ITS-90 to show its deviations to the density–salinity relation in the left figure below. In this figure, the magnetic float data is separated into density measurements that were explicitly performed in a closed cell⁶, thereby preventing evaporation of water during measurement, and into those that were putatively performed in an open cell, thereby allowing evaporation. If water evaporates from the seawater, depending on the duration and the sequence of measurements, the salinity and density increase. The densities for $S < 30$ are therefore systematically too high, which explains the upward scatter in deviations for $S < 30$ compared to that for $S \geq 30$. Thus, only the data with the smaller deviations, i.e. the lower points in left figure, in this salinity range should be considered to investigate the dependence on salinity. The right figure shows the deviations of the left figure normalized using the mean deviation of the measurements made with a closed cell (without evaporation). The smaller deviations for $S < 30$ highly correlate with the zero-line suggesting a linear dependence on salinity.

Note that the density data for $S = 40$ is not shown, as these measurements may be affected from the preparation by evaporation; actually, these densities, i.e. the salinities, were found to be too high, when combining the density data of Millero et al. and Poisson et al.⁶

⁶ JPOTS: Background papers and supporting data on the international equation of state of seawater 1980, Unesco Division of Marine Sciences, web: <http://unesdoc.unesco.org/images/0004/000473/047363eb.pdf>, 1980.

⁷ Millero, F. J., Gonzales, A. and Ward, G. K.: The density of seawater solutions at one atmosphere as a function of temperature and salinity, *Journal of Marine Research*, 34, 61–93, 1976.

⁸ Poisson, A., Brunet, C. and Brun-Cottan, J. C.: Density of standard seawater solutions at atmospheric pressure, *Deep-Sea Research*, 27A, 1013–28, doi:10.1016/0198-0149(80)90062-X, 1980.

⁹ Feistel, R.: A Gibbs function for seawater thermodynamics for -6 to 80°C and salinity up to 120 g/kg, *Deep-Sea Research*, 55, 1639–71, doi:10.1016/j.dsr.2008.07.004, 2008.

¹⁰ Feistel, R.: A new extended Gibbs thermodynamic potential of seawater, *Progress in Oceanography*, 58, 43–114, doi:10.1016/S0079-6611(03)00088-0, 2003.

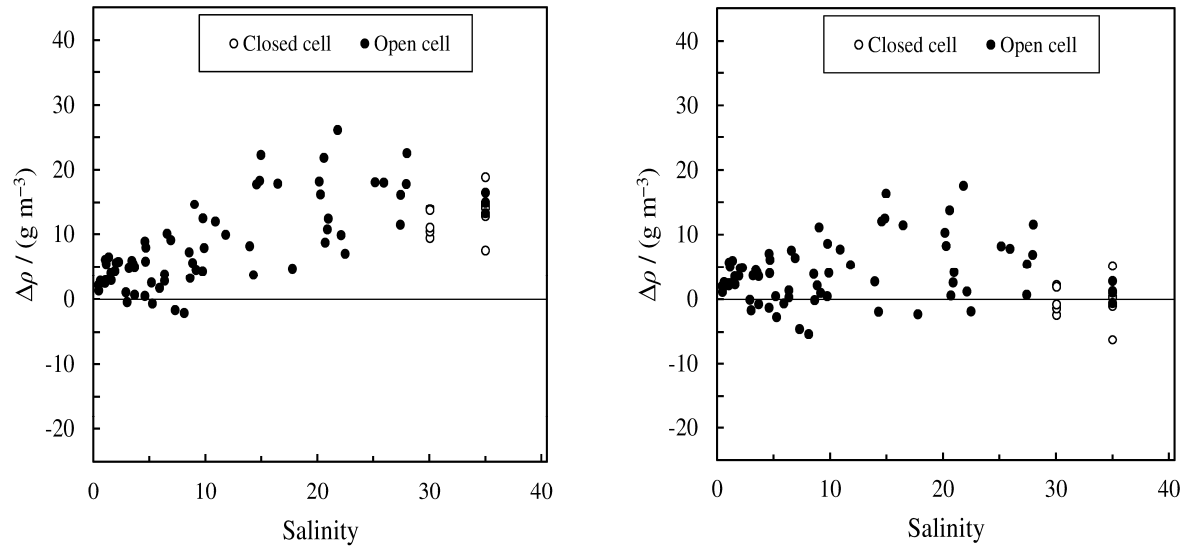


Fig. Deviation of densities obtained from standard seawater using a magnetic float densimeter by Millero et al.⁶ from the density–salinity relation (M. et al. minus DSR). Absolute deviations (a) and salinity-35-normalized deviations (b).