

## A New Method of Salinometry

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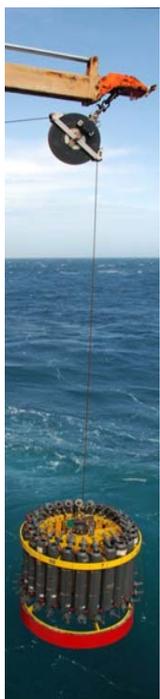
### Abstract

This paper addresses the importance of performing salinity measurements of deep sea water without warming samples to room temperature. Practical salinity of deep water samples were measured by the inductive dual cell ratiometric Micro-salinometer MS-310 that was set in the range of deep-water temperatures (2-5°C). This setup eliminates the need to wait for salinity samples to balance with room temperature and therefore provides immediate and direct Rosette-to-Salinometer sample salinity measurements. Not only does this method provide a fast CTD cast validation, but it also delivers a more sophisticated method of practical salinity measurements without loss of the original physical-chemical composition of the seawater samples.

Recent testing of this method onboard CCGS “Hudson” in the North Atlantic (Orphan Basin) involved direct measurements of 11 doubled, deep water salinity samples just after the CTD cast. The results of the low temperature direct salinometry show that the value of the practical salinity of samples in comparison to the standard Autosal technique, decreased in 0.003 with standard deviation 0.001. What is remarkable is that these measurements correlate well with the onboard CTD *in situ* salinity (doubled sensors SBE-911) within 0.000, with standard deviation 0.001. The difference in salinity between the Autosal and MS-310 could be even larger in other water masses with different compositions from that of Atlantic seawater.

The key question is this: Which salinometry technique better represents the thermodynamic property of natural seawater and is better harmonized with CTD measurements? The answer can be found by using the complementary implementation of the new salinometry method in relation to the existing practice of onboard measurements and observational reasoning that happen in different parts of the World Ocean. Finally, a new salinometry technique is well able to answer the questions raised by reformers of the PSS-78. The conductivity method of salinity determination is still not implemented in full in practical salinometry and there is therefore potential for improvement.

### Introduction



High precision laboratory measurements of practical salinity by salinometers (defined hereafter as “salinometry”) is the cornerstone method for validation of the CTD-systems. It involves transferring units of conductivity from the IAPSO standard seawater to a conductivity sensor using the Practical Salinity Scale 1978 [1]. Autosal technique, internationally accepted and WOCE program recommended as the only standard method of salinometry, has kept a strong position in oceanographic measurements for more than 25 years. It became a well-standardized and reliable method of high precision salinometry in calibration laboratory practice and on-board salinometry[2]. However, the limitation of the Autosal bath temperature range and request for thermal equilibrium of the samples with the Autosal bath temperature, creates controversy between the conductivity of the seawater measured by CTD *in situ* and conductivity ratio of the taken salinity sample measured by Autosal in laboratory. The difference in the temperatures of measurements and, what is also important, the significant time delay between CTD cast and Autosal sample salinity measurements can produce counted differences in the practical salinity measurements between them. This can occur especially in waters with non-ideal ionic composition of seawater and also in waters with a high level of dissolved gases and suspended organic and non-organic matter [3,4]. On the one hand, this can be the deep water masses with high concentration of the

dissolved gases and non-oxidized organic matter, which could be oxidized and degassed during thermal stabilization period of the samples. On the other hand, any inner seas and coastal waters, especially in estuaries, have specific ionic composition, with different than PSS-78 conductivity-temperature relation. These different conditions of seawater samples will produce differences in the practical salinity measured by CTD and Autosal. These uncertainties will depend on the difference between *in situ* temperature and the Autosal bath set temperature, because conductivity-temperature relation of these waters will not comply with the PSS-78. Also the presence of organic matter in a sample can change the composition of the seawater sample during the thermal stabilization period. A sample, for preference, should be considered as a living substance that needs to be measured *in vivo*, that is, just after getting the sample on board. Otherwise, the awkward situation occurs where the CTD-system could perform, *de facto*, more accurate salinity measurements than the existing Autosal salinometry technique that is used *de jure* as the standard technique for on-board conductivity calibration. In practice, on-board salinometry and the evaluation of the CTD data becomes a big issue during cruises and requires a lot of attention for the final evaluation and acceptance of CTD-data. Usually it is not because of problems with CTD performance, but rather, is due to uncertainties of *in situ* and *in vitro* seawater salinities measured in different conditions. Harmonization of the measurements between a CTD and a salinometer is the keynote to improvements of the practical salinity measurements. First step needs to be done in resolving the uncertainties and limitations of the PSS-78.

As the saying goes, the new is a well-forgotten old. Before the introduction of the PSS-78 in 1930-1960s, the ratiometric salinity bridges were the only instruments to provide on-board laboratory measurements of the salinity samples. In conditions of undefined CT-S relations, the ratiometric principle gives a direct ratio conductivity value of the seawater sample measured against Standard Seawater at the same bath set temperature as it was *in situ*.

The first apparatus of this kind was constructed in 1930 by the US National Bureau of Standards, and was known as the Wenner-Smith Salinity Bridge (Fig.1). In 1956, A.Bradshaw and K.Schleicher (WHOI, USA), like R. Cox (NIO, UK), in 1958, had developed laboratory salinometer made of 2- electrode conductivity cells in a bath of oil equipped with heating, refrigeration, an electronic control of temperature, and a resistance bridge. Salinity was measured by comparing the conductivity of the measured sample with that of standard sea water after balancing of the temperature of the two samples in the oil bath. These instruments were large, complex, heavy (more than 200 kg) and thus non-marketable. However they reached the necessary precision of  $\pm 0.003$ .

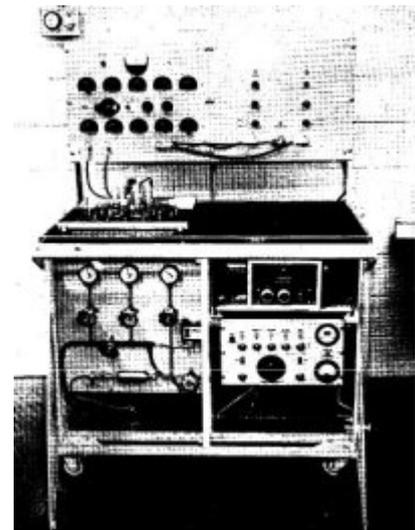


Figure 1. Wenner Smith Salinity Bridge

Unfortunately for science, after the introduction of the PSS-78 and Autosal technique, laboratory salinity measurements became more routine technical measurements with the main goal of verifying and calibrating CTD-systems. Nowadays there are no real salinity bridges on board research vessels and no information collected about ratio conductivity of the freshly delivered salinity samples, measured at *in situ* temperature. In the presence of the global processes of the changing physical-chemical composition of seawater, such data are very important for improving salinity measurements.

The aim of this paper is to present a renewed version of old-fashioned method of salinometry based on new measuring technology in order to meet a modern request in accuracy of the salinity measurements.

## Method

### 1. Micro-Salinometer MS-310

The MS-310 Micro-Salinometer (Figure 2) is based upon a concept in which conductivity of the sample of seawater is directly and simultaneously compared with the conductivity of a sample of standard seawater[5]. The dual cell removes the need for highly stable bath temperatures, and the cells are surrounded by a well-stirred oil bath to ensure thermal uniformity. Every sample is therefore standardized, and the standard itself is enclosed in quartz glass to preserve the integrity of the reference measurement for weeks. By giving a direct reading of  $R_t$  against the reference, the instrument gives a rapid confirmation of the accuracy of a CTD with low operating costs. Standardisation of the instrument can be performed easily on ship board or in the field using IAPSO Standard Seawater.



Figure 2 A view of the MS-310 and the software control panel.

### *Measurement principle*

The MS-310 uses two similar inductive conductivity measuring channels to obtain a direct measure of the conductivity ratio  $R_{tm}$ .

The two cells are maintained at the same temperature in a well-stirred oil bath.

$$R_{tm} = C_{sample} / C_{standard}$$

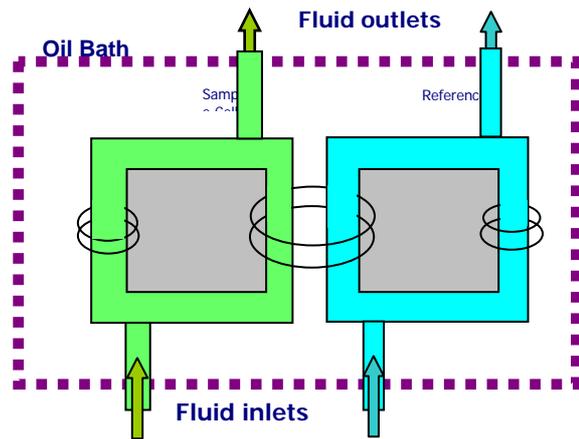
where:  $C_{sample}$  is the conductivity of the sample  
 $C_{standard}$  is the conductivity of Standard Seawater.

To calculate the salinity, the value of  $R_{tm}$  from the measurement is multiplied by the  $K15$  of the standard seawater to obtain a true value of  $R_t$ . This value of  $R_t$  is then applied to the accepted equation to calculate the salinity according to the Practical Salinity Scale -1978 [1].

This equation needs the temperature of the sample and this is measured from the temperature bath.

## Specifications:

Power: 115/230VAC; 12VDC, 10VA  
Communications: RS-232 or USB via adapter  
Size: 305mm×280mm×200mm  
Weight: 4.6kg (bath empty), 6.6kg (bath filled)  
Cell Volume: 15ml, typical sample <100ml  
Bath volume: 2.0 litres  
Bath oil: Marcol-7  
Operating Temperature: 0°C to +35°C  
Standardisation: IAPSO Standard Seawater  
Settling Time: ~2 minutes typical  
Set Up Time: 30 minutes typical  
Temperature:  
Sensor: Thermistor  
Accuracy:  $\pm 0.002$  °C  
Resolution:  $< 0.00005$  °C  
Drift:  $< 0.002$  °C/year  
Conductivity Ratio Rt:  
Sensor: Inductive Conductivity Cell  
Range: 0.05 to 1.2  
Linearity:  $\pm 0.00005$   
Repeatability:  $\pm 0.00005$   
Stability:  $\pm 0.00005$  / 24hrs  
Derived Practical Salinity (defined by PSS-78)  
Range: 2 to 42  
Accuracy:  $\pm 0.002$  within  $\pm 4$ °C of temp. at standardization  
Resolution:  $< 0.0002$



## 2. Method of measurements.

In May 2009 the MS-310 was taken in CCGS “Hudson” HUD2009011 cruise in the North Atlantic (Orphan Basin/Knoll). Onboard equipment included SBE-911 CTD with doubled C,T sensors and Autosal Guildline 8400B. CTD data QC procedure required taking at least 8 salinity samples at each cast to verify performance of the CTD according to standard Autosal technique. In addition, duplicated samples were taken from one deep water bottle at each cast for MS-310 technique samples salinity measurements. Control check of performance of the MS-310 was done with 10 duplicated samples, taken from different casts and depths and measured by Autosal and MS-310, set in one laboratory . Also, the same samples were measured by MS-310, set at 13°C in wet lab.

After the MS-310 was set in a cooling chamber in wet lab, to achieve MS-310 bath temperatures close to the deep waters temperatures (2-5°C). Actually, MS-310 design allowed to set the MS-310 measuring chamber into any convenient thermally controlled bath or climatic chamber with thermal stabilization at least  $\pm 1$ °C. MS-310 was standardized with IAPSO Standard Seawater at set low temperature. Duplicated salinity samples had been measured within 30minutes after CTD cast was done without heating of a sample. All salinity measurements data were achieved with MS-310 RBR Windows software and recorded with automatic “Save” option in the data file.

## Results

The results of seagoing testing of a new method of salinometry and comparison of this method with standard Autosal technique shown in Figures 4-6.

On the Fig.4 shown the results of control check of performance of MS-310 and Autosal in the same laboratory conditions, using the Autosal sampling preparation technique. On this diagram also shown differences between measurements of salinity samples by MS-310, directly after CTD cast S<sub>ms</sub>(fresh) and after thermal stabilizing of samples at room temperature, i.e. using Autosal samples preparation technique (S<sub>ms</sub>(as)).

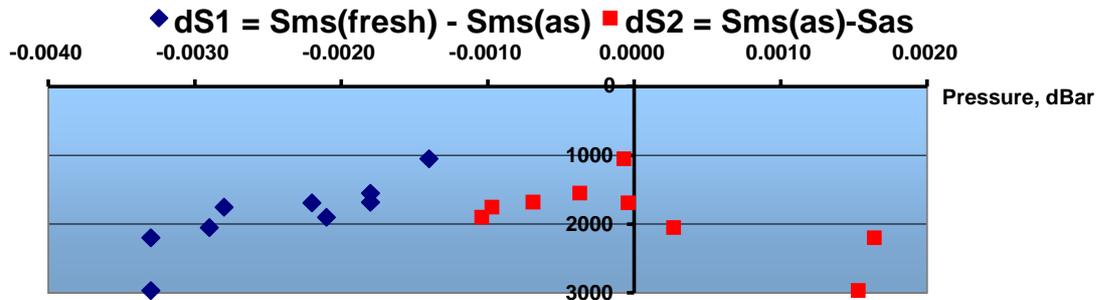


Figure 4. Control check duplicated salinity samples practical salinity residuals for conditions:  
 dS1 – fresh samples measured by MS-310 vs samples, measured by MS-310 with Autosal samples technique: Mean (dS1)=-0.0024; STDev=0.0008  
 dS2 – samples, measured by MS-310 vs Autosal, set both in one lab and using Autosal samples technique: Mean (dS2) = 0.0000; STDev=0.0010

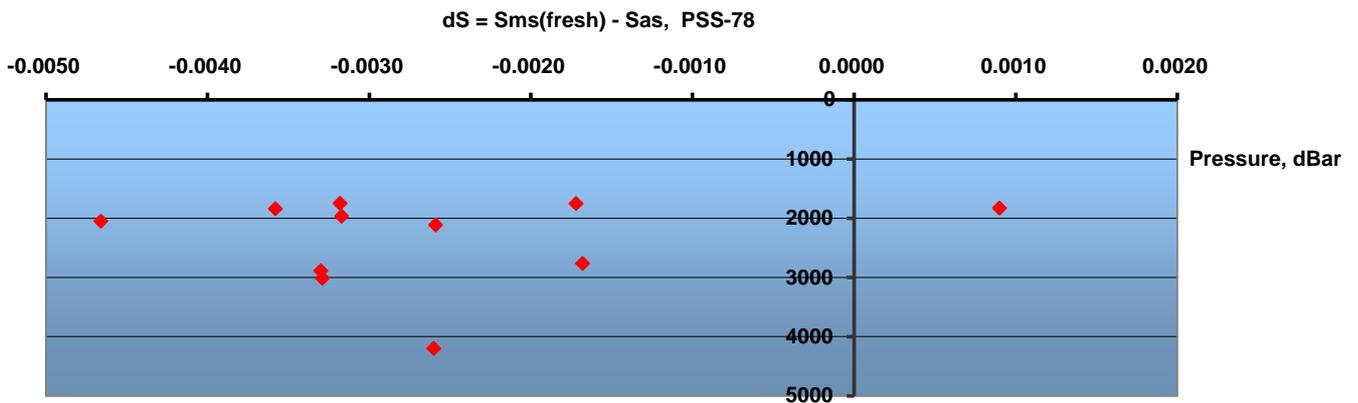


Figure 5. The practical salinity residuals for duplicated salinity samples, measured by MS-310 directly after cast and by standard Autosal technique: Mean(dS) = -0.0026 ; STDev = 0.0014

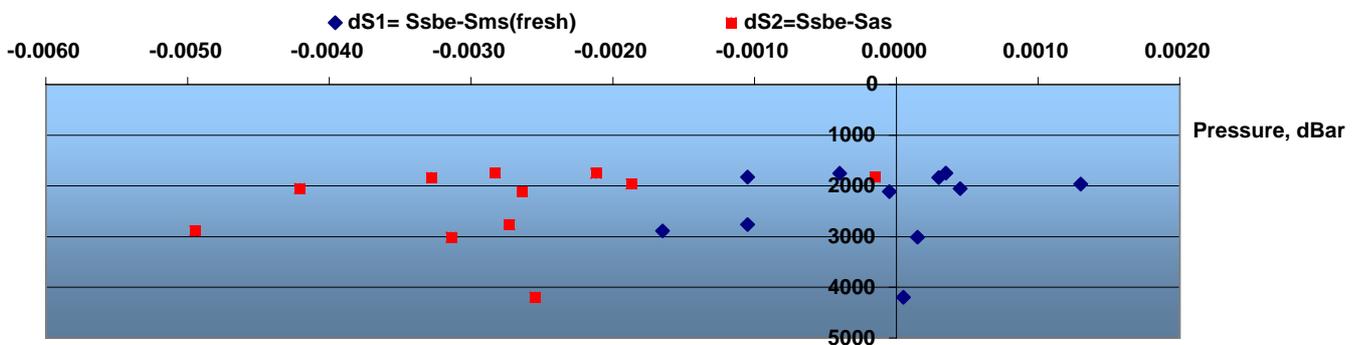


Figure 6. HUD2009011 cruise SBE-911 CTD averaged salinity vs different salinometry methods samples salinity residuals:  
 dS1 – SBE-911 vs direct cold samples, measured by MS-310 method: Mean (dS1) = -0.0001; STDev(dS1)=0.0008  
 dS2 – SBE-911 vs standard Autosal method: Mean(dS2) = -0.0028; STDev(S2)=0.0012

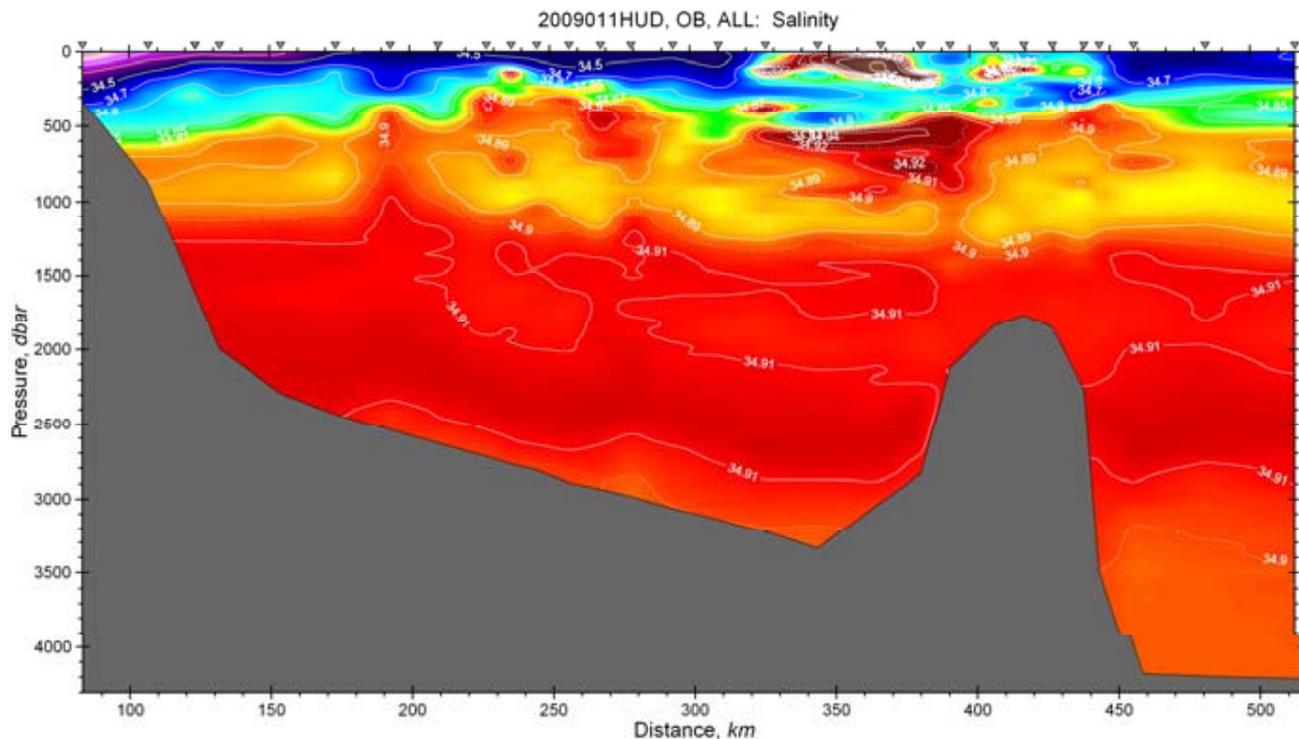


Figure 7. HUD2009011 Salinity distribution along Orphan Basin transection, where deep water salinity samples were measured with using the new and the standard methods of salinometry.

## Conclusions

1. A global process of changing the physical-chemical properties of seawater requires implementation of the new methods (or renewing the old ones) in a practice of salinity measurements.
2. Changing of the temperature and bio-physical-chemical properties of salinity sample during the room thermoequalization period, following the Autosal technique, could countably change derived practical salinity of the sample. Requirement for accuracy in precision CTD salinity measurements ( $\pm 0.002$ ) is in controversy with uncertainties of the current standard method of onboard salinometry.
3. The best approach to onboard salinometry would be in performing the precision salinity samples measurements shortly after a CTD-cast, at temperature close to *in situ* temperature.
4. The optimum technique for direct salinometry is ratiometric dual-cells salinometers (salinity bridges), which does not have strong requirements for the salinometer bath temperature stabilization.
5. Recent testing of the new method in the North Atlantic using Micro-Salinometer MS-310 as ratiometric salinometer, shows that even for the well circulated North Atlantic deep waters, differences between practical salinities, measured using two different salinometry techniques can reach up to 0.005.
6. The results of the test show that there are no significant differences between *in situ* salinity measured by recently calibrated precision CTD and direct “fresh” *in vivo* samples salinity measured by MS-310 at close to *in situ* temperature.

7. Autosal deep water samples salinity data were always higher than CTD *in situ* measurements (up to 0.005) and can misleadingly be interpreted as pressure affect on conductivity cell. We can suppose that during thermo-equalization period, Autosal samples changed their physical-chemical properties and became more conductive. It must be highlighted that these changes were not caused by evaporation of sample and control test proved it.

8. Conductivity measurements are volumetric by definition, i.e. reflect electrical property of specific volume of the seawater sample. Variations in specific volume due to different concentration of dissolved gases *in situ* and in sample after storage (thermo-equalization), can produce differences in measured conductivities, which is not taken in account in the PSS-78. Introduction of the TEOS-10 with current standard method of onboard salinometry, will not resolve the problem in precision salinity measurements because it is still based on primarily undefined conditions for conductivity-temperature measurements of the salinity sample.

9. Introduction of the new method of salinometry in the operational practice of the onboard salinometry will improve accuracy of the practical salinity measurements defined by the PSS-78. In the future, no matter how oceanographic community will define salinity – *absolute, reference or practical*, - salinity measurements must be operationally - practical, methodically-correct and instrumentally - accurate.

## Literature

1. UNESCO technical papers in marine science №37 “Background papers and supporting data on the Practical Salinity Scale 1978”
2. Stalcup, M.C., “Salinity Measurements” WHP Operations and Methods, 1991
3. Park, K., Burt, W.V “Electrolytic conductance of Sea Water and the Salinometer”, Journal Oceanographic Society of Japan, Vol.21, №2-3, 1965
4. Brewer, P.G., Bradshaw, A. “The effect of non-ideal composition of sea water on salinity and density”, Journal of Marine Research, Vol.33, №2, 1975
5. Shkvorets, I., Johnson, F. “Ocean Performance of the New MS-310”, Sea Technology, 10, 2006

## Acknowledgements

We thank Rick Boyce and CTD team from the Bedford Institute of Oceanography for help in salinity sampling for the MS-310 and collecting the CTD and Autosal data in the HUD2009011 cruise onboard CCGS “Hudson”.

The Micro-Salinometer MS-310 was developed and manufactured in RBR Ltd. in order to satisfy customers needs in small and reliable salinometer for calibration of the RBR’s CTD-systems in any environment conditions. Thank all RBR staff for their support and contribution to the development and manufacturing of the MS-310.

## For further information

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