Autolab Inductive Salinometers
Model 601 Wk. III

Notes on problems with their use

N.I.O. Internal Report No. A. 41

August 1969
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Introduction

The Medoc '69 cruise to study the formation of Mediterranean bottom water in the Gulf of Lyons presented a unique opportunity to test methods of salinity measurement because for part of the time the water was very uniform (potential temperature constant to within a few thousandths of a degree C) over a very large volume extending tens of km horizontally and some two thousand metres in depth. Thus, salinity determinations by different ships using different methods and equipment could be accurately compared. Further, the salinity was in the region of 38%, which is comparatively far from that of Copenhagen Water (at approximately 33%), and this shows up clearly some types of error which might be only marginally detectable with the salinities usual in the North Atlantic.

The results showed some disturbing features, there being both considerable internal inconsistencies in some equipments and systematic differences between the values obtained with different types of equipment. For example, the table shows the mean values of salinity obtained by various methods in the same water.

Systematic differences in measurements of salinity of Deep Mediterranean Water during the Medoc '69 expedition.

Note: comparison of standard sea water used by "J. Charcot" with that used by "Discovery" gave agreement within ± 0.001%, using the N.I.O. Thermostat Salinometer.

<table>
<thead>
<tr>
<th>Ship taking sample</th>
<th>Instrument used for analysis</th>
<th>No. of samples over which mean in Col. 4 taken</th>
<th>Mean salinity and scatter</th>
<th>Other information</th>
</tr>
</thead>
<tbody>
<tr>
<td>R.R.S. Discovery</td>
<td>Autolab salinometer</td>
<td>28</td>
<td>38.4152 ± 0.003</td>
<td>Salinometer on board ship. Values obtained after the faults described in this report were corrected</td>
</tr>
<tr>
<td></td>
<td>N.I.O. Thermostat salinometer. Serial number 15</td>
<td>24</td>
<td>38.4107 ± 0.003</td>
<td>Some samples were duplicates of those above. Measurements in lab. at N.I.O.</td>
</tr>
<tr>
<td>J. Charcot</td>
<td>N.I.O. Thermostat salinometer Serial number not known</td>
<td>31</td>
<td>38.4047 ± 0.002</td>
<td>Salinometer aboard the ship</td>
</tr>
<tr>
<td>R.V. Atlantis II</td>
<td>W.H.O.I. Thermostat salinometer</td>
<td></td>
<td>38.414 ± 0.003</td>
<td>Salinometer aboard ship. Selected deep samples. Preliminary values for part of cruise only.</td>
</tr>
</tbody>
</table>

The error figures quoted are the standard deviations of the measurements from the mean.
In analysis of duplicates of the same sample on the Jean Charcot and on the Atlantis II gave a difference of \( \cdot008\% S \).

The British ships were using Autolab Model 601 Mk. III inductive salinometers, and when R.M.S. Discovery returned to Toulon for a day or two in March 1969, it was decided to try to determine why the two instruments aboard (one of which had previously been in use on H.M.S. Hydra) were giving poor results. Some days were spent on this work, and the conclusions are presented below.

Findings

(1) One salinometer gave erratic results: in several cases duplicates varied by more than \( \cdot01\% S \) (the worst discrepancy being \( \cdot04\% \)). It was observed that a small amount of water was leaking out past the stirrer seal. This evaporated to the point of crystallisation. However, on some occasions it was observed that this water was being transferred back into the cell. A simple calculation shows that this contamination is quite sufficient to cause the observed errors.

(2) The temperature compensation was then checked. It proved to be extremely difficult to get good compensation curves. (This had also been our experience in the lab. ashore). In the end the trouble was traced down to bubble formation, often so slight as to be almost unnoticeable. In these cases it was observed that when the stirrer was stopped, there was a very slight sheen on the inside of the top of the cell. Samples were therefore de-gassed by placing the sample bottle in a water-bath at about 60°C for half-an-hour, after which consistent temperature compensation curves could be obtained. (Note: de-gassing this way may alter the salinity slightly and should only be used when checking temperature compensation).

(3) Some errors in one instrument were due to the terminal block in which the leads from the bridge are connected to the measuring head. Very slight electrical leakage between certain mounting pins can be serious: in the case of the most sensitive pair, 10Ω would cause appreciable errors. However, leakage resistance to earth is comparatively unimportant, and an earthed screen has been incorporated which should cause most leakage currents to go to earth. This screen had become disconnected from earth and the salinometer readings changed appreciably when it was re-connected. The precise pattern of use of these pins is critical, but no diagram of it is given in the handbook and if for any reason the connections had to be removed for servicing they might well be re-connected in the wrong positions. Also, the block is in an inherently damp situation and as far as we could see no anti-tracking treatment had been used. It seems to us that this block should be fabricated from sheet metal using glass or ceramic lead-throughs for the mounting pins. In this way all resistive leakage must go to earth.

(4) A possible cause of incorrect ratio readings between the standard and a sample of different salinity is a faulty phase balance of the bridge, though how serious this is depends on the goodness of the phase adjustment of the phase-sensitive rectifier. We have found that the phase balance is liable to quite large and usually inexplicable changes, but no convenient arrangements are made to allow it to be monitored or the phase adjustment of the rectifier checked. As a minimum, the output of the balance amplifier should be brought to a test point on the front panel.
Conclusions

It is disturbing to find so many possible causes of error in an instrument which is so widely used. What in some ways makes matters worse is that the errors caused are all of the order of 0.01%. This means that in most circumstances the errors are not big enough to be obvious, but are big enough to be significant.

We feel that undetected bubble formation is only too likely in normal use. Many samples when taken will contain a quantity of nitrogen which is more than enough to saturate them at lab. temperature. Thus, if the recommended procedure is followed and the sample is left for several hours to reach lab. temperature, it will probably be slightly super-saturated. It is then put in the cell where it is stirred vigorously and slightly warmed, so that one would expect slight bubble formation. Our tests showed this to be significant in its effect on the measurement but not visually obvious. It may account for the difficulty we sometimes encounter in getting agreement between duplicates, though we know of no case where this has been proved.

The stirrer seal is probably not a serious cause of trouble when it is in good condition. After considerable use, however, it is likely to deteriorate and cause considerable errors before it is detected.

Readily accessible test points should be provided so that the correct operation of the instrument, particularly with regard to phase balance, can be checked as a routine.

The measuring-head terminal board is a potential source of trouble and we feel that the design of this is capable of improvement.

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August 1969