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Use of the Goldberg Refractometer as a Salinometer for Biological and Geological Field Work

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ABSTRACT

The Goldberg Refractometer (American Optical Co., model 10402) has been tested as a potential field salinometer. The instrument has a range of 0 to 220°/oo and an accuracy of about one ppt. Although it is inaccurate relative to titration and conductimetric salinometers, the Refractometer has the advantages of temperature compensation, small size, small sample requirements, large range, and low cost.

Introduction. It has long been known that the refractive index of a solution is directly proportional to its total dissolved solids. Three factors have discouraged the use of refractometers to measure salinity: (i) variation in the refractive index with temperature, with the degree of variation depending, in turn, on concentration (Williams et al. 1964); (ii) insufficient accuracy for density determinations usable in hydrodynamic computations; (iii) expense of refractometers having accurate temperature controls.

Most salinometers have been designed for the extreme accuracy (± 0.02°/oo) and limited range (0–50°/oo) required by physical oceanographers. However, many marine biologists and geologists require accuracies of only ± 0.1 to 1.0°/oo but higher ranges. For example, the salinities in Texas bays range from zero to over 70°/oo and occasionally exceed 100°/oo; and tidal pools are sometimes more than 200°/oo. Thus, a new, relatively inexpensive, temperature-compensated refractometer that has a wide range and moderate accuracy has been tested as a potential field salinometer.

Instrument. Refractive indices were determined with a Goldberg Refractometer (American Optical Co., model 10402). According to the manufacturer, this instrument has "a unique hermetically sealed hollow prism, filled with a stable liquid, [which] changes index with temperature to compensate ... for

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temperature changes of the sample.” This liquid prism apparently has a thermal coefficient of refractive index that is approximately equal but opposite to that of aqueous solutions. The precision of the compensation is discussed further under Error, p. 167.

The instrument is 16 cm long and 3.1 cm in diameter. Its scale of refractive indices shows a range of 1.3730 to 1.3330, the lower limit being the refractive index of pure water at 20°C. The scale is also marked in refraction units of 0 to 400, representing 104 times the difference in refractive index between the sample, n, and pure water, n0, at 20°C, i.e. (n-n0)104. The instrument is zeroed with a sample of distilled water by adjusting a single screw so that the reading is 1.3330 (zero on the refraction scale). The only other adjustment is focusing the eyepiece. The sample used may be as small as one drop (0.02 ml).

**Calibration.** Seawater from the Gulf of Mexico at Aransas Pass, Texas, was diluted with doubly distilled water and evaporated until a series of 130 samples whose salinities ranged from 3.6 to 217.9‰ was obtained. A pipetted volume of each sample was titrated against silver-nitrate solution using a Metrohm automatic titrater and Potentiograph. Three sizes of samples were used, depending on salinity. Replicate titrations showed an analytical error of ±0.05 ml. The corresponding errors in salinities are shown in Table I.

<table>
<thead>
<tr>
<th>Number of samples</th>
<th>Sample size (ml)</th>
<th>Salinity range (ppt)</th>
<th>Analytical error (ppt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>10</td>
<td>0–40</td>
<td>±0.1</td>
</tr>
<tr>
<td>35</td>
<td>5</td>
<td>40–80</td>
<td>±0.2</td>
</tr>
<tr>
<td>60</td>
<td>2</td>
<td>&gt;80</td>
<td>±0.5</td>
</tr>
</tbody>
</table>

The chlorosity, calculated directly, is plotted versus refraction in Fig. 1. The chlorosity was divided by density to give chlorinity (Cl), which was converted to salinity (S) by the standard equation, \( S = 1.805 \times Cl + 0.03 \). Densities were determined by weighing 10-ml samples to the nearest milligram. It would take a weighing error of over 4 mg to effect an error of 0.1‰ in the final salinity. The maximum error in weighing would be ±2 mg and thus is insignificant. All measurements were made at room temperature (26°C). The only temperature-affected data were the densities; thus they were corrected from room temperature to 20°C so that they would correspond to the reading of the temperature-compensated refractometer. Salinity versus refraction is plotted in Fig. 2.

A comparison of Figs. 1 and 2 shows that the Refractometer readings are directly proportional to salinities (grams per kilogram); but the relation to chlorosity (grams per liter) involves a higher-order function. The proportion-
ality between salinity and refraction can be expressed in the straight-line equation:

\[ S = 0.55 \times (n - n_0) \times 10^4. \]  \( \text{(1)} \)

**Error.** The first source of error is in reading the scale. Maximum readability is to the nearest 0.5 refraction unit, \((n - n_0) \times 10^4\), with an error of ±0.5 (equivalent salinity ±0.3°/oo). Likewise, when a sample of distilled water and white light is zeroed, the refraction line cannot be accurately adjusted to 0.0, the reading error being as much as 0.5 scale units. This shows up in calibration as a nonzero, average deviation. This error can be corrected by adding the average deviation to the above equation as a y-intercept term; e.g., in the present calibration the resulting equation was:

\[ S = 0.55 \times (n - n_0) \times 10^4 - 0.3. \]  \( \text{(2)} \)
It is most unlikely that the temperature compensation of the instrument is perfect, because thermal coefficients of aqueous solutions change with both temperature and concentration. Although these changes are small relative to the coefficients themselves, the precision of the compensation was tested by taking refractometer readings on five samples at various temperatures. The results are plotted in Fig. 3. As a criterion for precision, a deviation from the mode of 0.5% was considered to mark the limit of acceptable temperature compensation. These limits are summarized in Table II.

<table>
<thead>
<tr>
<th>Salinity (ppt)</th>
<th>Limits of Effective Temperature Compensation</th>
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<tbody>
<tr>
<td></td>
<td>Lower</td>
</tr>
<tr>
<td></td>
<td>°C</td>
</tr>
<tr>
<td>100</td>
<td>11</td>
</tr>
<tr>
<td>74.5</td>
<td>18</td>
</tr>
<tr>
<td>41</td>
<td>23</td>
</tr>
<tr>
<td>34</td>
<td>22</td>
</tr>
<tr>
<td>31.5</td>
<td>23</td>
</tr>
</tbody>
</table>

These data show that the instrument should be used only in the 24-to-35°C range, but that this range increases at higher salinities by depression of the lower limit.
Figure 3. Effect of temperature on refractometer readings for five samples of Gulf of Mexico seawater. Salinities calculated from refraction: $S = 0.55 (n - n_0) \times 10^4$; limits of acceptable temperature compensation marked with parallel vertical dashes.
The standard deviation between titration salinities and salinities calculated from eq. (2) is 0.43°/oo, equivalent to ±0.9°/oo at the 95% confidence level. Since an average analytical error in titration of ±0.3°/oo contributes to this total error, the salinities determined with the Refractometer have a somewhat lower standard error. Inspection of Fig. 2 shows that the scatter of points increases with increasing salinity. The error in the most-used portion of the scale (below 70°/oo) is thus probably about 0.5 ppt. This is essentially the reading error, because temperature during calibration was essentially constant.

The increased error at higher salinities is due to three factors: (i) an increase in the analytical error with smaller samples (Table I); (ii) fuzziness of the line within the Refractometer at higher salinities, probably due to increased dispersion of the various wave lengths in white light with increased refraction; (iii) destruction of the assumed constant ratio of total salts to chloride ion with precipitation at higher salinities of carbonates and sulfates. Fifteen samples that had abnormally high deviations from the above ratio and contained obvious precipitates were not included in the calculation of standard deviation.

The salinity at which precipitation begins varies with the conditions of evaporation, from about 50 to over 100°/oo. By slow evaporation of still water, precipitation can be delayed until relatively high salinities are achieved. Agitation reduces the salinity of initial precipitation; and agitation with a carbonate substrate reduces it still further. This is a clear-cut example of supersaturation during evaporation. Precipitation tends to begin in naturally evaporated water at the lowest salinities, because concentration usually increases slowly, agitation is relatively high, and the substrate or suspended load usually contains abundant seed grains.

In the field, turbid water tends to obscure the reading slightly. This is rarely a serious problem, but it may be avoided by sampling with a hypodermic syringe containing a filter. Contamination must be avoided by rinsing the instrument with distilled water or with the new sample if a sufficient quantity is available. Two or three readings should be made, when possible, to check such contamination. Evaporation of the sample is no problem if the reading is taken in less than 30 seconds.

It is estimated that the total error from all the above sources is ±1°/oo up to about 70°/oo, and ±2°/oo above that.

Conclusions. The Goldberg Refractometer offers the following advantages:

i. Simple construction, permitting rapid salinity determinations, with data for a surface-water sample obtained and recorded in less than one minute.

ii. Low cost, the Goldberg Refractometer being much less expensive than conductivity salinometers or bench-type refractometers.

iii. Small size, enabling ease of transportation anywhere in the laboratory or field.
iv. **Large range**, of 0 to 220°/oo, which is greater than the range of other salinometers.

v. **Accuracy** of ±1°/oo up to 70°/oo, and of ±2°/oo above 70°/oo, which is sufficiently accurate for most biological and geological field work but not for physical oceanography.

vi. **Simplification**, with temperature compensation, making unnecessary either control of, or correction for, temperature variations, the results being as if obtained at 20°C.

vii. **Processing small samples**, including those from the smallest micro-environments, e.g., interstitial water from bottom samples or cores.

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