Electrolytic Conductance of Sea Water and the Salinometer*

(Part 2)

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4. Precision of salinometers

The reproducibility of results by the various salinometers is more precise than that of the chlorinity method. All of the electrode-type and inductive salinometers give precisions better than 0.01% S. Since it is very important that the salinity results obtainable by the chlorinity titration and conductivity methods be comparable, many intercalibration tests have been made (COX, 1963b; BERTHOLF, 1963; ROCHFORD, 1964; BERTHOLF and BELLER, 1964). Several examples are shown here.

(1) Comparison between chlorinity titration and conductivity methods

Cox's (1963b) intercalibration among the precise chlorinity titrations and various salinometers were in excellent agreement (Table 7).

The differences observed between the two methods are practically within the precision of the titration method.

Table 8 gives a comparison of the salinity determination by two different salinometers (University of Washington type, and inductive salinometer) and by the chlorinity titration method. The average difference between the inductive salinometer and the titration methods was 0.01% S, which is within the precision of the titration technique.

(2) Comparison among various salinometers

Cox's (1963b) comparison among four different types of salinometers, all electrode type, gave a maximum difference of 0.015% S and average random error of the less than $\pm 0.004\%$ for the samples in salinity range $33.36 \sim 37.97\%$ (Table 7).

Table 7. Results of analyses on various salinometers (from Cox, 1963b).

Salinity	Salinometer						
by titration	A	В	С	D	E	F	Average
33.362	33.356	33.354	33.369	33.364	33.369	33.361	33.362
33.861	33.858	33.857	33.868	33.865	33.867	33.860	33.863
35.149	35.148	35.147	35.147	35.147	35.144	35.149	35.147
36.438	36.438	36.436	36.436	36.443	36.437	36.439	36.438
37.972	37.963	37.964	37.960	37.975	37.965	37.999	37.965

Salinometer A-N.I.O. type No. 5 at Wormley.

B-N.I.O. type No. 2 at Lowestoft.

C-Woods Hole No. 1 (25°C thermostat).

D-Woods Hole No. 2 (15°C thermostat).

E-University of Washington.

F-I.M.C. (South Africa).

† This high value is due to the calibration of this instrument being based on the extraporeted formula of THOMAS *et al.*, (1934). This value is omitted from the calculation of average values and random errors.

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Table 8. Comparison of salinity analysis by different salinometers and AgNO₃ titration (from PARK and BURT, 1963). Unit: ‰ S.

OSU Inductive salinometer	Univ. of Washington salinometer	Difference	AgNO ₃ Method	Difference
30.999	31.006	0.007	30.98	0.02
32.018	32.021	0.003	32.00	0.02
33.002	33.008	0.006	33.01	0.01
34.008	34.015	0.007	34.01	0.00
34.998	35.012	0.014	35.00	0.00
36.007	36.016	0.009	35.98	0.03
	Constant err Random erre			difference 0.01

The data of Park and Burt (1963) comparing the University of Washington salinometer with the inductive salinometer gave a constant error of 0.008% and a random error of $\pm 0.003\%$. Since the international standard sea waters used to standardize the two salinometers were not certified for conductivity but for chlorinity, the constant error of 0.008% may contain the descrepancies within the standard waters (See standard sea water section). The random error of 0.003% is about the precision specified by the manufacturer of the inductive salinometer.

The U.S. Navel Oceanographic Office conducted two controlled tests of various types of salinometers to compare the instruments and techniques used. The first test was held in May 1962 and the second in November 1963 (BERTHOLF, 1963; BERTHOLF and BELLER, 1964). The second test is described below.

Three separate batches of homogeneous samples (30, 35, and 39 % S) were prepared and put into Jena glass ampoules. Thirty salinometers at 15 different laboratories obtained ten replicas of each salinity. The analyses were made on the same date (20 November 1963). As a further check on repeatability, each salinometer made 20 determinations of its own substandard sea water. Eighteen inductive salinometers, five University of Washington type, four National Institute of Oceanography (British) type, two Woods Hole type, and one Wenner-Smith-Soule type salinometer (manufactured by U.S. National Bureau of Standards), were used in the test.

The frequency distribution of salinity values

for the three batches tested is shown in Figure 10. Comparison factors for the salinity intercalibration are given in Table 9. Although standard deviations obtained from the experiment are between ± 0.004 and ± 0.007 % S (Table 9), some salinity values are considerably scattered (Figure 10).

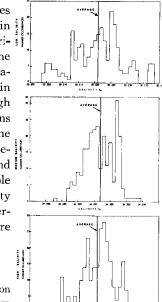


Fig. 10.
Frequency distribution of salinity values from identical samples.

(From BERTHOLF and BELLER, 1964).

Table 9. Comparison factors for salinity intercalibration experiment (from BERTHOLF and BELLER, 1964).

Comparison factor	Salinity %-Control samples			
Comparison factor	Low	Medium	High	
International Association of Physical Oceanography (I.A.P.O.)	30.220	34.497	38.861	
Overall average value of all bridges	30.221	34.497	38.856	
Lowest average bridge value	30.205	34.488	38.346	
Highest average bridge value	30.238	34.504	38.867	
Difference	00.033	0.016	0.021	
Average deviation of individual bridge from IAPO values	±0.006	±0.004	±0.006	
Standard deviation	± 0.0072	± 0.0043	± 0.0069	

(3) Comparison between shipboard and shore analyses

The salinometer intercalibration tests described heretofore have been carried out under optimal shore laboratory conditions. The differences shown in Figure 10 are mainly the variations among the salinity bridges. It is therefore, very important that the variations resulting from different collecting and storing procedures and conditions, including shipboard analytical conditions, be examined. We report our test results with an Australian inductive salinometer (PARK and BURT, 1963).

For shipboard test, we used a small constant temperature bath on gimbals to warm sea water samples to 22°C. Sea water samples were collected in 350 ml citrate bottles and immediately placed in the bath. After ten minutes, they were analyzed for salinity beginning with the surface samples. Within one hour after the Nansen bottle cast, conductometrically analyzed salinity values were obtained.

A set of identical samples was analyzed at the campus laboratory a week later. Table 10 gives a portion of the results. The average difference between the shipboard and shore analyses for 70 duplicate samples was 0.003 % S. No apparent decrease in reproducibility of salinity analysis due to the ship's motion was encountered.

Table 10. Comparison of shipboard and shore salinity analysis. Cruise: ACONA 6209-D; station NH-53; September 1962. (From PARK and BURT, 1963).

Depth		Salinity (‰))
(m)	At sea	Shore	Difference
0	32.113	32.114	0.001
10	32.267	32.272	0.005
20	32.264	32.268	0.004
30	32.505	32.511	0.006
50	32.621	32.625	0.004
60	32.720	32.721	0.001
65	32.795	32.796	0.001
80	33.089	33.091	0.002
100	33.521	33.521	0.000
150	33.885	33.886	0.001
200	33.939	33.941	0.002

Although OSU's test results were excellent, only a single salinometer was used. Further shipboard tests comparing various salinometers aboard their respective ships are needed in order to understand the extent of the combined variations resulting from the sampling and salinity bridges.

Effects of biogeochemical processes on salinometer precision

Variances in the ionic ratios among the major constituents in sea water undoubtedly affect salinometer precision. These variances may be divided into two groups: (1) inherent and (2) biogeochemical.

The first group consists of random and patchy distribution of ions having no correlation with apparent biogeochemical processes. For instance, Cox (personal communication and in UNESCO, 1963) finds that magnesium concentration shows no correlation with depth but does exhibit strong regional trends. His analyses illustrate that all deep Mediterranean samples possess a Mg/Cl ratio well below the average, while surface samples from the North Atlantic are all high. The variations found in magnesium could account for about half of the observed chlorinity/conductivity (Figure 2) variances.

Contrarily, dissolution of calcium carbonate in the deep oceans increases both the calcium and the alkalinity with depth. Photosynthesis and respiration affect the carbon dioxide system in sea water, which in turn affects the concentrations of ionic and nonionic species of the carbon dioxide system. These are some of the examples of the effect of biogeochemical processes.

In this section we briefly describe the effects of carbon dioxide, calcium carbonate dissolution, and photosynthesis and respiration on the electrolytic conductance of sea water.

(1) Effects of the carbon dioxide system

Any addition of molecular carbon dioxide causes an adjustment among the dissolved carbon dioxide species, and hence a decrease in pH of the water. Such a change is produced in the sea by biological activity and by exchange with the atmosphere.

The effect on the conductance of the addition and removal of carbon dioxide gas from sea water was investigated by BRADSHAW of Woods Hole Oceanographic Institution, GRASSHOFF of Institut für Meereskunde der Universität Kiel, and PARK and WEYL of Oregon State University. The WHOI and OSU data are given in Figure 11 (PARK et al., 1964). The data of GRASSHOFF (personal communication), shown in Table 11, agrees very well with that of BRADSHAW, PARK

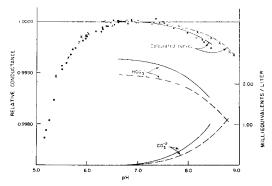


Fig. 11. Changes in the electrical conductance versus pH in sea water with carbon dioxide addition, with the calculated HCO₃⁻ and CO₃⁻² concentrations in sea water as a function of pH. (From PARK et al., 1964).

Table 11. Changes in pH and conductance of sea water by carbon dioxide (from GRASSHOFF, personal communication).

pН	Relative conductance	Computed salinity (‰)	Difference of salinity (%)	Remarks
8.4	1.00046	35.018	-0.012	Constant chlorinity
8.3	1.00051	35.021	-0.009	
8.2	1.00058	35.023	-0.007	
8.1	1.00064	35.025	-0.005	
8.0	1.00068	35.027	-0.003	
7.9	1.00071	35.029	-0.001	
7.8	1.00074	35.029	-0.001	
7.7	1.00075	35.030	0.000	
7.6	1.00076	35.030	0.000	

and WEYL.

From both Figure 11 and Table 11, it is apparent that systematic errors may be introduced in the conversion of conductivity to density or salinity if changes in the carbon dioxide system are not taken into consideration. The magnitude of changes in a typical oceanic pH range of 7.6 to 8.4 are a function of alkalinity (Figure 11), and they could be as 0.012 ‰ salinity equivalent (Table 11). The changes in the conductance are due to the transformation of bicarbonate to carbonate ions or vice versa (PARK et al., 1964). The bicarbonate ion is more conductive than its equivalent carbonate ion (PARK, 1964b).

When the pH of sea water is lowered below 7 by the addition of carbon dioxide gas, the

conductance decreases rapidly with decreasing pH (Figure 11). When conductance is plotted as a function of the concentration of molecular carbon dioxide, we find the conductance decreases linearly with increasing molecular carbon dioxide at a rate of 0.013 % per millimole per liter (Figure 12).

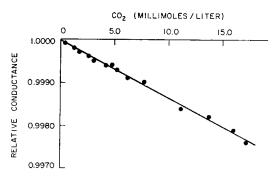


Fig. 12. Electrical conductance of sea water as a function of molecular carbon dioxide content. (From PARK et al., 1964).

The exact mechanism of the decrease in the conductance by uncharged carbon dioxide molecules has not been verified by experiment. PARK et al. (1964) attempted to explain it by partial molal volume of carbon dioxide in sea water. BRADSHAW pointed out that the increase in viscosity due to the increase in carbon dioxide content (OSTWALD and GENTHE, 1903) would account for the conductance decrease found in the measurements of PARK et al. (1964). Obviously more work is needed to understand the exact mechanism of the conductance decrease with the addition of uncharged carbon dioxide.

MIYAKE et al. (1964) calculated the magnitude of variance on the conductance due to the changes in the carbon dioxide species in the deep sea. Their estimation was based on Bradshaw's CO₂-conductivity relationship (in PARK et al., 1964), and Sugiura's total carbon dioxide determination obtained during the 1960 Japanese Deep–Sea Expedition. They found that a variance as much as 0.01 % salinity equivalent was induced by changes in the carbon dioxide species.

(2) Effect of dissolved oxygen

Recently BRADSHAW (personal communication)

carried out an experiment to measure the effect of dissolved oxygen on the conductance of sea water. His measurements with zero-alkalinity sea water (pH 5.8) at 15°C show that the addition of 1 millimole of oxygen to the sea water decreases the conductance by about 0.01 ‰ salinity equivalent. For a typical oxygen concentration range found in the ocean, 0 to 7 ml/l, the corresponding conductance change could be as large as 0.003 ‰ salinity equivalent.

The mechanism of the effect of oxygen may be similar to that of uncharged carbon dioxide.

(3) Effect of calcium carbonate dissolution

COX (personal communication, and in UNE-SCO, 1963) theoretically estimated the effect of carbonate dissolution. PARK (1964c) measured it experimentally. These two investigations show that the dissolution of calcium carbonate as calcium bicarbonate would increase the apparent salinity by about 0.01 ‰.

Cox's direct calcium measurements (UNESCO, 1963) for the sea water samples obtained in various oceans give a calcium/chlorinity range from 0.02132 to 0.2165, lower values for the surface and higher for deep-sea waters. The increase in ratio, if due to the dissolution of calcium carbonate in deep waters, would correspond to about 0.1 millimole CaCO₃ dissolution per liter of sea water. Independently, if we assume that the increase in specific alkalinity with the depth, from 0.12 to 0.13 meq/l (KOCZY, 1956), is due to carbonate dissolution, we obtain the same 0.1 millimole of carbonate dissolution per liter of sea water.

Park's experiment (1964c) consisted of dissolving onlite (aragonite) in sea water in the presence of excess carbon dioxide (Figure 13). The specific conductance of sea water was increased by about 6×10^{-5} ohm⁻¹cm⁻¹ per millimole of carbonate dissolved. The net increase in conductance is the result of the dissolution of the crystals as calcium bicarbonate, the hindrance effect of uncharged carbon dioxide on the conductance, and the transformation of some of the initial carbonate ions into bicarbonate ions. The first of these is the most important to the calculation of the effect of carbonate dissolution.

It should be stressed here that reglardless of

calcium carbonate dissolution in deep water, the chlorinity of the water will remain a conservative property. On the other hand, the increase in conductance due to the dissolution of carbonate minerals will compensate, in some degree, for the increase in density. Therefore, when a conservative property is needed, precise measurements of chlorinity should be used rather than the conductance. Furthermore, the conductivity/chlorinity ratio can be used to estimate the carbonate dissolution in deep waters.

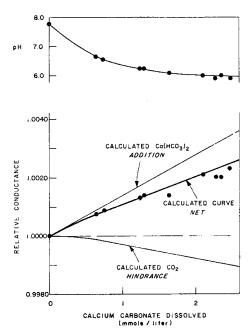


Fig. 13. Changes in pH and electrical conductance of sea water with calcium carbonate dissolution. (From PARK, 1964c).

(4) Effect of photosynthesis and respiration

During photosynthesis, the oxygen content of sea water increases and carbon dioxide content decreases. In a typical oceanic pH range from 7.6 to 8.3, photosynthesis is accompanied by an increase in pH and by the transformation of bicarbonate to carbonate ions. Both oxygen increase and carbon dioxide decrease favor a decrease in conductance.

On the other hand, during respiration, both oxygen decrease and carbon dioxide increase favor an increase in conductance. Therefore, photosynthesis will accompany a decrease in conductance, while respiration will be reflected in an increase.

In addition, we must consider the effect of ionized organic excretion by biological activities. When all of these parameters are wholly in-

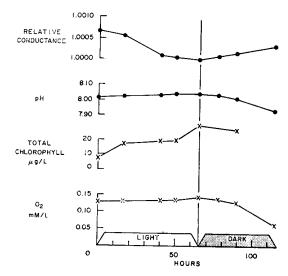


Fig. 14. Concurrent changes in electrical conductance, pH, chlorophyll and dissolved oxygen during the photosynthesis and respiration studies of marine diatom, *Skeletonema costalum*. (From PARK and CURL, 1965).

vestigated, we may be able to utilize conductometry in the estimation of photosynthesis and respiration. The realization of such a goal appears to be in the remote future, but this possibility should not be ignored in our future studies.

As an example, the effect of photosynthesis and respiration on the conductance of sea water is given by PARK and CURL (1965) (Figure 14).

6. International standard sea water

Cox showed clearly that the conductance of sea water varies substantially even at a constant chlorinity (Figure 2). It is, therefore, quite possible that standards having identical chlorinity posses different electrical conductances.

PARK (1964a) examined the anomalies between chlorinity and conductivity by comparing 12 different batches of international standards. His data are summarized in Table 12. He observed no systematic correlations between changes in salinity (conductometry vs. chlorinity) and pH, nor between salinity and the age of the standards (Figure 15). In general, salinities determined by the conductometric means are in good agreement with values computed from the certified chlorinities.

Table 12. Difference of salinity values computed from certified chlorinities and determined by conductivity measurements for twelve different batches of the international standard sea waters taking batch P₃₇ as a reference standard (from PARK, 1964a).

Batch number		ration ate	Certified chlorinity ‰	Computed salinity ‰	Salinity from conductivity ‰	Difference of salinity ‰	рН
P ₁₅	30/6	1937	19.393	35.034	35.032	0.002	7.90
P_{18} *	4/12	1949	19.376	35.004	35.016	0.012	7.92
P_{24}	6/5	1956	19.378	35.007	35.011	0.004	7.92
P_{25}	6/1	1957	19.378	35.007	35.007	0.000	8.09
P_{26}	8/12	1957	19.367	34.987	34.990	0.003	7.98
P_{29}	27/9	1959	19.370	34.993	35.010	0.017	8.06
P_{30}	28/2	1960	19.370	34.993	34.995	0.002	7.78
P_{31}	28/8	1960	19.375	35.002	35.002	0.000	7.90
P_{32}	8/1	1961	19.376	35.004	35.006	0.002	7.81
P_{35}	4/3	1962	19.373	34.998	35.004	0.006	7.72
P_{36}	23~24/9	1962	19.375	35.002	35.004	0.002	7.70
P ₈₇	16/12	1962	19.369	34.991	34. 99 1	0.000	7.90

^{*} P₁₈ contained white suspended material in its ampoule.

Salinometer used: Australian C.S.I.R.O. Inductive Salinometer.

Analysis temperature: 23.5°C~23.7°C. Date of analysis: 13 August 1963.

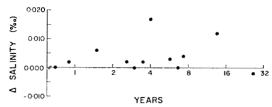


Fig. 15. Differences between salinity values computed from certified chlorinities and determined by conductivity measurements vs. the ages of the international standard sea waters, taking batch P₃₇ as a reference standard. (From PARK, 1964a).

Copenhagen standard sea water has a pH range of 7.7 to 8.1 (Table 12). This is somewhat lower than the surface pH, although the water is obtained from the surface layers of the Atlantic. The change implies that the pH of the water has changed during storage. If the changes in pH during storage are due to changes in carbon dioxide, then the conductance of the standards would increase during the storage (Figure 10). In order to overcome this problem, GRASSHOFF of Germany (personal communication) suggests that the pH of the standards be changed arbitrarily to about 7.7~7.8 before measuring the absolute conductivity and chlorinity and sealing.

Since use of the salinometer has become widespread, and since the conductivity-density ratio (Figure 4) of sea water is intrinsically more consistent than the chlorinity-density ratio (Figure 3), we need to know accurately the electrical conductivity of standard sea water. At present, both the Standard Sea Water Service and the National Institute of Oceanography (English) are actively working on the certification of the standards in conductivity as well as chlorinity.

7. Concluding remarks

As it has been and as it will be always, research in oceanography is international in scope. Together, but not a man alone, nor a country alone, we understand the description and the dynamics in the oceans. One good example of the cooperative effort is on the conductivity problem of sea water. The work began almost a century ago, and it still continues by many workers. Although this review paper reveals

the extent of our knowledge and our ignorance about the electrolytic properties of sea water, we sincerely hope that this article may help to focus the critical eyes of many coworkers throughout the world on one of the urgent problems in oceanography.

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