EFFECT OF DELAYED TITRATION ON THE SALINITY DETERMINATION

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Wüst (1932) has discussed the effect of storage on the chlorinity of samples. He compared the results from samples examined almost immediately at sea with those titrated in the shore laboratory after a considerable period of time. He concludes that there is a definite tendency for the chlorinity to increase on storing. The effect was largest with sample bottles that had been previously titrated and, therefore, no longer full; and least with full bottles on which the stoppers had been covered with paraffin wax. In the case of the incompletely full bottles the mean increase of chlorinity was 0.011‰ while in the case of the full bottles with paraffined stoppers it was only 0.002‰. For many purposes, as, for instance, the exploration of relatively unknown waters, such small differences can be of little importance but in the investigation of well known areas and, particularly, in cases where the seasonal and long period changes of the physical characters are sought, even such small effects may be of the same order of magnitude as those which are being examined.

It is frequently impossible and very often inconvenient to examine samples for salinity immediately. Further, a ship board laboratory seldom, if ever, reaches the same convenience for analysis as that found on shore. In connection with the present investigation of the fluctuations of the Gulf Stream and in consideration of the relatively homogeneous waters of the Sargasso Sea, small differences of salinity are obviously of considerable importance. It seemed desirable to determine whether the effect of storage is as great in this region as Wüst had found in his observations.

On 5th January 1939 at "Culver" station 106, samples were collected in the usual manner; but from 100, 496, and 905 meters, as many sample bottles as could be filled were obtained. The sample bottles had been carefully examined and washed with water from the same respective depths from a previous haul so that a small amount of rinsing with the actual sample was sufficient.

The titrations were performed in the manner set out by Oxner and Knudsen (1920) and the greatest care was taken to avoid errors. The apparatus was carefully cleaned to eliminate erratic drainage and the readings were made with a special burette magnified so that the interpolation of the last figure could have some degree of probability.

While many observers titrate to a definite color, the present worker has found from experience that such a procedure depends upon the observer's power to memorize the particular tint. This power is very variable in different workers and even in the same worker during different stages of the examination. The usual tendency is for the accepted end point color to become darker as fatigue sets in. Quite small changes in the light also effect the apparent tint. The procedure adopted here was to titrate until there was the first definite permanent *change in tint* as compared with standards. The possible effect of changing light was eliminated by using constant artificial illumination. The stock potassium chromate solution was freed from possible chloride contamination in the usual way by the addition of a drop of silver nitrate.

Before a sample bottle was opened, the stopper was rinsed with distilled water and wiped dry. The failure to observe this precaution is probably the cause of many anomalous salinity results.

A great deal has been said by various workers about the possibility of evaporation during examination. Wüst (1932) goes so far as to consider that this effect is so great as to eliminate the advantages of repeated titrations. The present author had found previously that samples which had come to temperature equilibrium with the laboratory showed no measurable change after being left open for four hours; and it would seem, then, that the erratic results often obtained in repeated titrations are more probably due to contamination through careless manipulation. When the sample undergoes vibration or shaking, as at sea, or is subject to large temperature changes, quite large salinity changes occur through a faulty stopper within quite a short space of time.

For the standardization of the silver nitrate, two tubes of normal sea water were used. The tubes were examined for small defects, such as small cracks in the tips, and then each tube was titrated three times. At the end of the titrations, three more titrations were carried out on each tube, thus giving six titrations for each normal water tube. In no case was there any appreciable difference between the means of the two sets of six titrations. This great care in standardization is necessary as any error in the standardization will appear in all the samples examined. One of the chief reasons why repeated examinations of a sample often add nothing to the accuracy is that there has been an error in standardization.

The first set of examinations on the samples was carried out a few hours after collection and each sample was titrated five times. It is well known to all analysts that, in repeated titration of the same

sample, there is an unconscious tendency to return the same figure. This is well seen in the ability of an analyst to obtain excellent agreement between duplicate titrations performed successively and failure when the duplicate examinations are separated by a time interval or by other examinations. In an attempt to minimize this effect the samples were examined successively so that the same sample appeared only every fourth time. Another advantage of this procedure is that any sustained trend, such as tiring of the observer, will be felt equally by each sample.

For the correction of the chlorinity and the conversion to salinity, Knudsen's (1901) data were used but, as the interpolation is too crude for the present investigation, smoothed curves were constructed for the required ranges. The samples were examined first in January; and subsequently in February, March, and April. On each occasion a new sample bottle was used and the process repeated in exactly the same manner. The results are given in Table I.[1]

TABLE I

Depth of sample (meters)	Salinity Determinations °/₀₀								
	Month of titration								*Grand Mean*
	January		*February*		*March*		*April*		
		Mean		*Mean*		*Mean*		*Mean*	
100	36.588		36.579		36.600		36.577		
	36.601		36.599		36.586		36.596		
	36.594		36.593		36.579		36.600		
	36.585		36.587		36.581		36.575		
	36.592		36.583		36.604		36.582		
		36.592		36.588		36.590		36.586	36.589
496	36.326		36.324		36.333		36.314		
	36.309		36.338		36.326		36.331		
	36.330		36.311		36.320		36.335		
	36.332		36.317		36.318		36.335		
	36.327		36.329		36.337		36.323		
		36.325		36.324		36.327		36.328	36.326
905	35.191		35.169		35.220		35.196		
	35.197		35.217		35.215		35.176		
	35.202		35.203		35.174		35.196		
	35.210		35.201		35.193		35.174		
	35.179		35.195		35.198		35.188		
		35.196		35.197		35.200		35.186	35.195

[1] The results are given as salinity ‰. Except in the mean values, the last figure is almost certainly without significance.

It can be seen immediately that there is no general trend of the samples on storing. In no case does the difference between the grand mean for the sample deviate by 0.01‰ salinity from any monthly value, and in only one case, for the April examination of the 905 meter sample, is this value approached. If this value is omitted the extreme range of the four monthly means for any one sample is less than 0.005‰ salinity. A statistical examination[2] of the data shows that the differences between means for months for the same sample are without significance.

A similar examination of the effect of storage was made with samples collected in April and stored until May. Here again, it was found that storage did not effect the salinity of the sample.

Storage, then, does not effect the salinity value of samples if due care is taken in their collection and storage. It should be pointed out that this conclusion has been established for the Bermuda region only. Whether it is true for other areas is still unknown. It is possible that in waters in high latitudes where the spring plankton is often very dense, and in places where stored samples are subjected to great climatic changes, this may not be so, and an examination of this possibility seems desirable.

These results should not be taken as justification for postponing titration without adequate reason; where there is any question of the satisfactory nature of the sample bottles, delay in titrating may produce enormous errors. But, provided this possibility does not arise, the effect of storage is negligible.

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[2] The statistical method used was that described in "An Introduction to Modern Statistical Methods" by Paul R. Rider, John Wiley & Sons, New York, 1939, pp. 132–137.