

14 July 1937

NRL Report No, P-1381

NAVY DEPARTMENT  
BUREAU OF ENGINEERING

Resistance-Temperature Curves  
of Salinity Solutions

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Number of Pages: Text - 6      Plates - 4

Authorized by: BuEng let.S65-5/L5(4-23-Ds) of 27 April 1936.

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Distribution: BuEng (5)

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## INTRODUCTION

### (a) Authorization

1. This work was authorized by Bureau of Engineering letters, references (a) and (b). Other references pertinent to the work are listed as references (c) to (h) below.

- Reference: (a) BuEng let.S65-5/L5(4-23-Ds) of 27 Apr.1936.  
(b) BuEng let.S65-5/L5(11-12-Ds) of 9 Dec.1936.  
(c) Supplementary General Specifications for Machinery, SGS(65)-131a, dated 15 Apr.1936, "Salinity Indicator Equipment."  
(d) "Salinity or Impurity Determination of Boiler Feed Water," J.Am.Soc.Naval Eng. 39, 658 (1927).  
(e) Material Testing Laboratory, Navy Yard, New York, Report No. 2319 dated 5 Dec.1933.  
(f) F. M. Dole, "Principles of Experimental and Theoretical Electrochemistry."  
(g) Carnegie Institution of Washington, Publication No. 63.  
(h) International Critical Tables, Vol.6, page 230.

### (b) Statement of Problem

2. The object of this work was to prepare curves giving the resistance of salinity solutions as a function of temperature for use in calibrating salinity indicators. This required the determination of the resistance of solutions containing 10-, 5-, 2-, 1-, 0.5-, 0.3-, and 0.1 grains of sea salt per gallon of solution over a temperature range from 50° F to 210° F, a wider range of temperatures than had been employed in obtaining the resistance curves in reference (c).

### (c) Known Facts Bearing on the Problem

3. Electrical salinity indicator systems have been developing in the Naval Service for many years. The earlier work is summarized in an article by Mr. Huey, reference (d). As Naval engineering advanced, the need for more accurate instruments and better data for use in calibrating them arose, and the Material Testing Laboratory, Navy Yard, New York, determined resistance-temperature curves for salinity solutions (reference (e)). Numerous measurements of the electrical conductivity of sea water solutions have been made by hydrographers but few of these have been with solutions as dilute as required in the Naval Service.

### (d) Theoretical Considerations

4. The solutions with which these measurements were made are classed chemically as dilute solutions of mixed strong electrolytes. The physical-chemistry theory of dilute solutions of single electrolytes has been well established. The present theory, the Debye-Hückel-Onsager theory (reference (f)), does not permit the exact prediction of the resistance of the solutions of mixed salts

found in sea water, but certain parts of the theory can be used to check the correctness of experimentally measured resistances. The theory was used for this purpose in the present work.

(e) Narrative of Original Work

5. The first measurements at this Laboratory were made with a standard Wheatstone bridge system on salinity solutions contained in glass flasks, using a Navy standard salinity cell of the Leeds and Northrup type furnished by the Sperry Gyroscope Company. It was soon found that the brass portions of the cell seriously contaminated the solutions and made accurate measurements impossible. Glass cells of the standard Washburn type were then tried, the electrodes being of platinized platinum. It was found that with the more dilute salinity solutions and, especially, at the higher temperatures, the glass walls of the cells dissolved so rapidly as to greatly reduce the resistance of the salinity solutions and hence to make accurate measurements impossible. It was then suggested that a special salinity cell be constructed having a platinum lining to minimize contamination. Upon authorization of the Bureau of Engineering (reference (b)), such a cell was designed and fabricated by this Laboratory, the platinum lining being made by the J. Bishop and Company Platinum Works. The cell was similar in design and construction to one which had previously been used by Professor A. A. Noyes (reference (g)), in determining the conductivity of pure salt solutions at high temperatures. The special cell was used in making the measurements recorded below. These measurements were made on salinity solutions containing from 10 to 0.1 grain of sea salt per gallon of solution over a range of temperature from 50° to 200° F.

METHODS

(a) Preparation of Materials

(1) Salinity Solutions

6. Navy standard sea water is an arbitrarily chosen solution having the following composition:

| <u>Navy Standard Sea Water</u>                       |  |
|--|--|
| <u>Substance</u>                                     | <u>Weight, Grains per<br/>Gallon of Solution</u> |
| Sodium chloride (NaCl)                               | 1419.4 grains/gallon                             |
| Potassium sulphate (K <sub>2</sub> SO <sub>4</sub> ) | 49.1 " "   |
| Calcium sulphate (CaSO <sub>4</sub> )                | 73.4 " "   |
| Magnesium sulphate (MgSO <sub>4</sub> )              | 76.9 " "   |
| Magnesium chloride (MgCl <sub>2</sub> )              | 199.5 " "  |
| Sodium bromide (NaBr)                                | 3.2 " "  |
| Sodium iodide (NaI)                                  | 0.3 " "  |
| Silica (SiO <sub>2</sub> )                           | 0.7 " "  |
| Iron oxide (Fe <sub>2</sub> O <sub>3</sub> )         | 1.1 " "  |
| Aluminum oxide (Al <sub>2</sub> O <sub>3</sub> )     | 1.4 " "  |

Navy standard sea water is most conveniently prepared by using the following weights of salts:

Laboratory Navy Standard Sea Water

| <u>Substance</u>                     | <u>Weight, grams per liter of solution</u> |
|--------------------------------------|--|
| NaCl                                 | 24.337                                     |
| MgSO <sub>4</sub> ·7H <sub>2</sub> O | 3.870                                      |
| MgCl <sub>2</sub>                    | 2.955                                      |
| CaSO <sub>4</sub> ·2H <sub>2</sub> O | 1.588                                      |
| KCl                                  | 0.676                                      |
| KBr                                  | 0.0630                                     |
| KI                                   | 0.0056                                     |

A solution so made does not contain the silica, alumina, and iron oxide, but is otherwise identical with the standard; the contribution of these to the conductance of the solution is negligible. In making the standard sea water solution, analytical reagent chemicals were used. These were dissolved in conductivity water obtained from the National Bureau of Standards. In making the dilutions, volumetric glassware accurate to the certification tolerances of the Bureau of Standards was used. From the standard sea water, a solution containing 1,000 grains of sea salt per gallon (Solution "A") was prepared by diluting 54.79 ml. of the standard to 1,000 ml. with conductivity water. From Solution "A" the 10-, 5-, 2-, 1-, 0.5-, 0.3-, and 0.1 grain solutions were prepared by appropriate dilutions with conductivity water.

(2) Apparatus

7. The special platinum lined conductivity cell is shown in Plate 1. It was made of a steel shell and lined with pure platinum which was spot welded at a few places to the shell. The inner platinum covered steel electrode was insulated from the outer electrode by a fused quartz cup. To make the cell liquid-tight at the inner electrode and at the junction between the top and the body of the cell, washers made of rings of annealed pure gold were used. Only the smaller inner electrode was platinized.

8. The special Wheatstone bridge circuit employed in making the resistance measurements is diagrammed in Plate 2. It comprises a Campbell-Shackelton shielded ratio box, shielded Leeds and Northrup resistance boxes, a 1000 cycle oscillator as the source of current, and an audio amplifier with a standard Navy radio headphone as the detector.

9. To control the temperature, an air thermostat was used. Temperatures were measured with a six junction iron-constantan thermocouple calibrated against Bureau of Standards certified thermometers.

(b) Description of Experiments

10. In each experiment the conductivity cell was carefully rinsed with the solution to be measured, then filled with the solution and placed in the thermostat. When temperature equilibrium was

attained, the resistance and temperature were measured. The temperature was then raised, and when equilibrium had again been reached the resistance and temperature were measured. This process was repeated until the highest temperature was reached. The system was then cooled, the cell filled with a new solution and the procedure repeated.

#### DATA OBTAINED

##### (a) Discussion of Errors

11. The errors to which work of this type is subject may be classified as follows: (1) electrical, (2) chemical, (3) temperature, (4) cell constant, (5) water correction.

(1) Electrical. Precision in the determination of resistance by alternating current bridge measurements depends upon the use of a technique, the theory and practice of which is well established; in measuring electrolytic resistances, refinement of this technique is required. The accuracy of measuring electrolytic resistance depends upon the frequency of the current employed. Current passing through an electrolytic solution causes polarization which increases the measured resistance of the cell. This polarization, and hence the error caused by it, diminishes as the frequency of the current increases. To minimize the polarization error, 1000 cycle current having a suitable wave form was used. The polarization error is large with bright platinum electrodes but is reduced by coating the electrodes with platinum black. In the present work the small inner electrode was platinized, but the outer electrode, because of its greater relative area, was left bright. It is believed that the electrical errors in this work approximated 0.1% with the more concentrated solutions.

(2) Chemical. By the use of pure reagents and precision voltmetric apparatus, the chemical errors were minimized. The accuracy of the dilutions was checked by chemical analysis by the Laboratory's analytical chemist, Mr. L. Singer. It is considered that the chemical errors approximated 0.2%.

(3) Temperature. The temperature coefficient of resistance of salinity solutions amounts to about 1% per degree F. Hence, if resistance measurements, whether aboard ship or in a laboratory, are to be made to this accuracy, the temperature must be measured to less than 1° F. In the present measurements, the temperature was controlled to about 0.1° F, a possible error of 0.2% thus resulting.

(4) Cell Constant. The cell constant was determined with .01 N potassium chloride solution at room temperature. This solution is too concentrated to give a satisfactory measurement of the cell constant for use with solutions in the range of resistance of the salinity solutions, but it is the most dilute of the standard Parker solutions, (reference (h)). Further, no standard solutions are available for temperatures above about 85° F., and as the cell constant changes with temperature, owing to expansion of the steel and platinum, an error is introduced into the cell constant by the

lack of suitable means of determining it at high temperatures. More serious, the range of resistance required to be measured is so great that a single cell cannot adequately cover the range. Precision in the determining of resistance of the salinity solutions, whether aboard ship or in the laboratory, would require the use of one cell for the less dilute solutions and another cell having a lower cell constant for the more dilute solutions. This is, of course, not feasible aboard ship and was not considered practical for these measurements. Uncertainty in the cell constant introduces an error believed to approximate 0.2% at the higher concentrations.

(5) Water Correction. The greatest error of all in these measurements is due to uncertainty as to the amount of current conducted by the water itself. In solutions of sea salt containing 10 grains or less of salt per gallon, an appreciable fraction of the total current passing through a conductivity cell is carried by the water itself, the remainder of the current being carried, of course, by the ions from the salts. With the very highest purity water available, in a 10-grain solution, about 0.1% of the current is conducted by the water at room temperature, while in a 0.1-grain solution 11% of the current is carried by the water. If good laboratory conductivity water is used in making the solutions, in the 10-grain solutions, 0.4% of the current is conducted by the water, while with the 0.1 grain solution 30% is carried by the water ions. With ordinary distilled water, this may be as high as 50% at room temperature. Since there are no data available on the conductivity of the water itself in the Naval Service, uncertainty as to the conductance value to be chosen for the water introduces an error into the measurements which becomes quite large at the higher dilutions even at low temperatures. With increasing temperature this error becomes larger, first, because data on the conductance of pure water at high temperatures is meager and poor and, second, because the temperature coefficient of conductance of water is higher than that of the salts alone.

#### DATA - Curves

12. The curves of Plate 3 show the conductivity of salinity solutions using a good grade of distilled water. Owing to the conductance due to the water itself and to the high temperature coefficient of this conductance, the curves at the lower concentrations have a much greater (negative) slope than do those for the higher concentrations, and each curve has a different slope. For an electrical salinity indicating system accurately to indicate the salinity at low concentrations, therefore, the system would have to have a different temperature compensator for each concentration in the dilute range. The additional complexity of the circuits needed to make this possible and the added expense which this entails are not believed to be justified. Hence, it is suggested that a set of rather arbitrary curves be made as a standard for calibrating salinity indicators. Such a tentative set is shown in Plate 4 in which the curves for the 0.5-, 0.3-, and 0.1- grain solutions are drawn with the same slope as that of the 1- grain solution and adjusted to have the same resistances at 130° F as the curves of Plate 3. A salinity indicating system calibrated to the curves of

Plate 2 would indicate the presence of 0.1- grain of salt in the water at high temperatures when actually there was present less than 0.1- grain; but at low temperatures with 0.1 grain indication there would be somewhat more than 0.1 grain of salt in solution. At 130° F the readings would of course be correct. The choice of 130° is arbitrary and was made as being half of the range 50° - 210° F; other temperatures could be chosen to give a better approximation to a given set of engineering conditions. The curves of Plates 3 and 4 are based upon the use of a conductivity cell having a cell constant of 0.100 at all temperatures in the range covered.

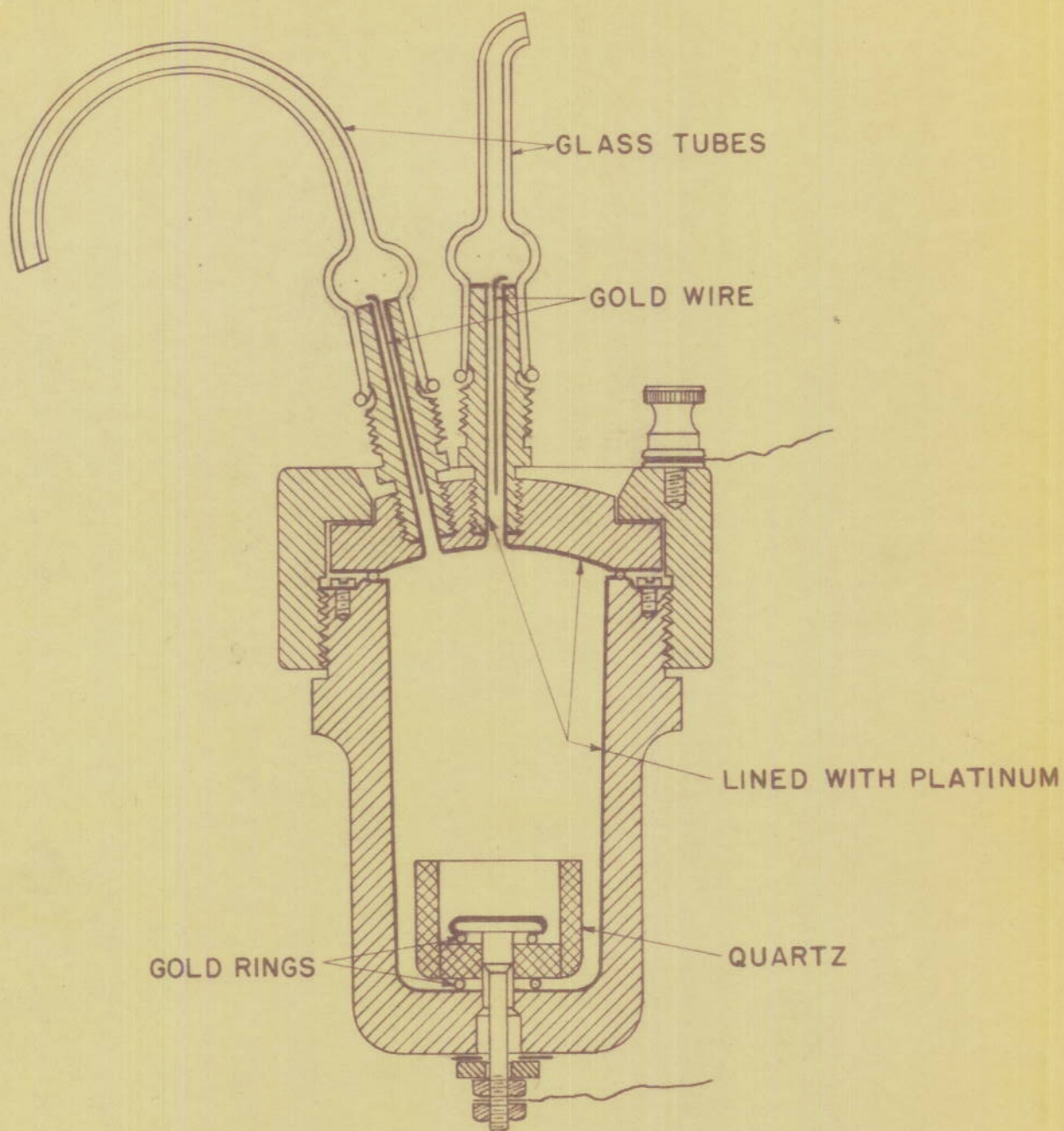
#### OPINIONS

13. In referring to salinity solutions the term "chlorinity in grains per gallon" is used interchangeably with the term "grains of salt per gallon." Actually, a solution made up according to the specification of reference (c) to have a salinity of 10 grains contains 10 grains of sea salt per gallon of water, but much less than 10 grains of chlorine per gallon. It is therefore considered that the term "chlorinity" should not be used and that the unambiguous expression "grains of sea salt per gallon" should be employed instead.

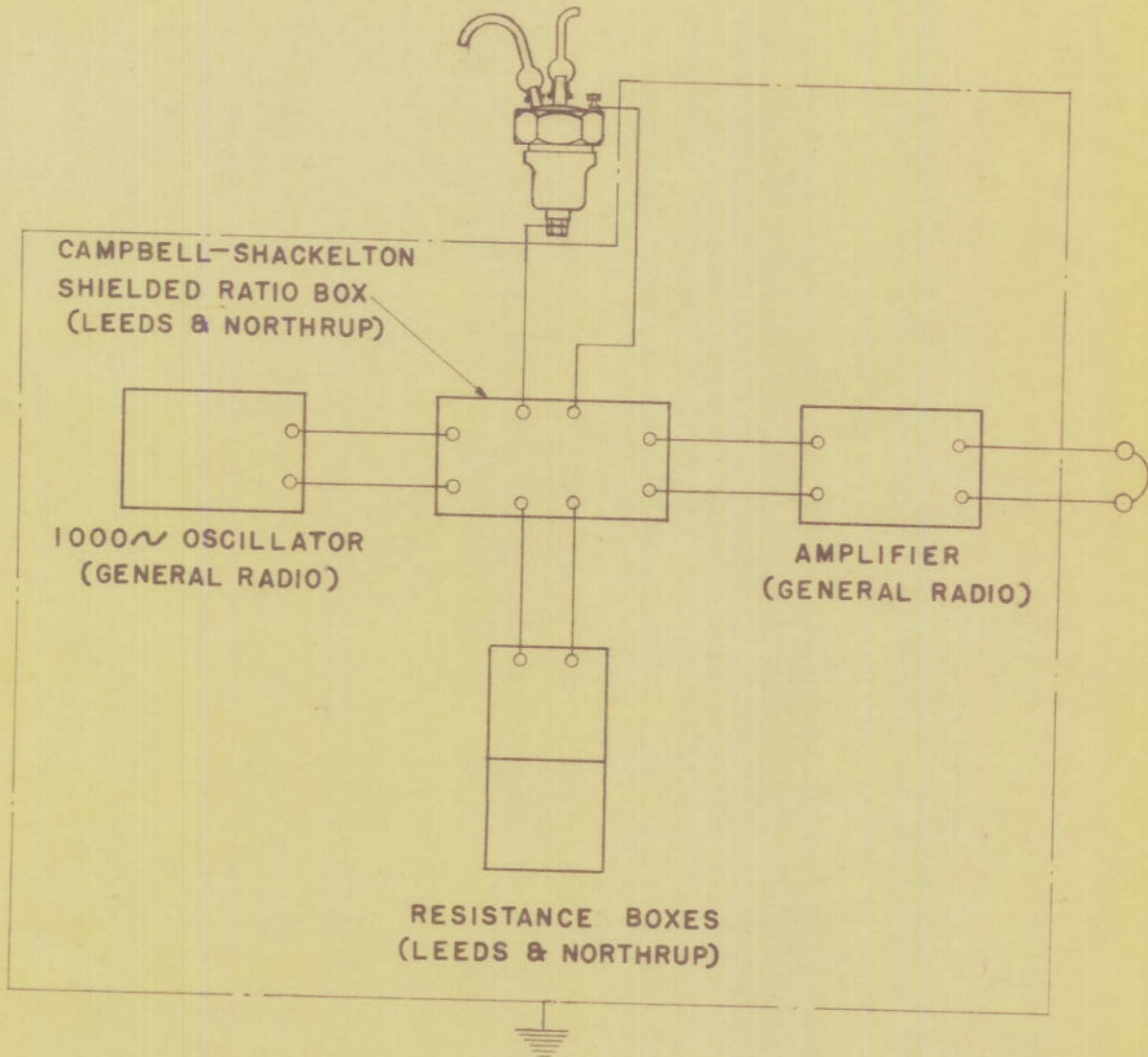
#### RECOMMENDATIONS

14. It is recommended:

- (a) That in par. D-7c of reference (c) the arithmetical error "... dilute 55.25 ml of standard sea water to 1,000 ml" be changed to read "54.79 ml of standard sea water to 1,000 ml."
- (b) The term "chlorinity" be not used and that salinity be expressed in terms of "grains of sea salt per gallon."



CONDUCTIVITY TEST CELL



APPARATUS FOR MEASURING  
CONDUCTIVITY OF SOLUTIONS