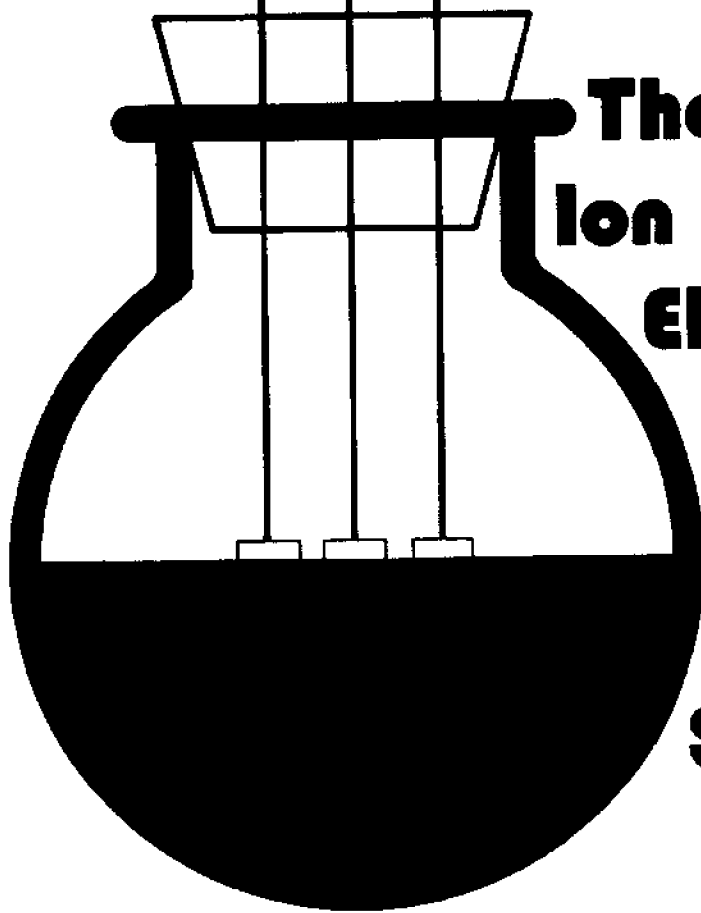


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# The Use of Ion Specific Electrodes for Chemical Monitoring of Marine Systems

**Part II by Richard Srna**

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The Use of Ion Specific Electrodes  
for Chemical Monitoring of Marine Systems

Part II

A Rapid Method of Detecting Changes  
in the Relative Concentration of Chloride  
and Divalent Ions in Seawater

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## INTRODUCTION

At the University of Delaware, as part of a Sea Grant sponsored project to demonstrate the feasibility of economically growing shellfish in a recirculating seawater system, a number of analytical techniques are being evaluated for potential use as monitors of water quality (Srna et al., 1973).

The concentration and ratio of major ions in the culture water of a mariculture system which contains a large number of organisms may change drastically as a result of processes involving assimilation, precipitation, accumulation, and evaporation (Stumm and Morgan, 1970). Since large quantities of calcium and magnesium carbonate are incorporated into the shells of molluscs during growth and it has been shown that a change in the ratio of calcium and magnesium ions in the culture water can induce "narcosis" in shellfish (Galtsoff, 1964), we felt that it was particularly important to have a single method of analysis for divalent ions in our mariculture system. We chose to consider recently developed ion specific electrode techniques as a means of analyzing for seawater ions.

We considered the potassium, chloride, and calcium divalent ion electrodes. The potassium electrode is not suitable for seawater analysis because other ions in seawater which are present in relatively high concentrations interfere with the determination of the potassium ion (Orion, 1969). The calcium divalent and chloride ion specific electrodes (Orion, 1965,

1966, 1967) also respond to other ions in seawater but to a much lesser degree than the potassium ion electrode, so our efforts focused on evaluating these three electrodes.

The theory, apparatus, techniques, and applications of ion selective electrodes in natural waters have been reviewed in an excellent monograph by Whitfield (1971) and will not be repeated in this communication. In general, the analyst has three methods to choose from when measuring the concentrations of ions in natural waters: titration, standard addition, and concentration calibration. Each of these methods has its advantages and limitations.

For the analysis of a complex multicomponent electrolyte solution such as seawater, the titration technique involves finding a very specific titrant or precipitating agent for the ion being analyzed.

The standard addition technique requires that a small volume of a solution of much higher concentration than the ion being analyzed be added to the unknown, and that the change in millivolt readings recorded by the electrode be measured. Implicit in this method is that the relative amount of complexation in the solution before and after the standard addition be the same, and that a means can be found to correct for the presence of any interfering ions.

The concentration calibration method involves preparing a standard curve of electrode potential in millivolts for a series of solutions of known concentrations. Then the electrode potential of a solution containing the ion in an

unknown concentration is measured, and the concentration of this unknown solution is evaluated by referring the measured millivolt potential back to the standard curve.

We selected the concentration calibration technique of analysis after some preliminary work with the standard addition and titration methods; but since seawater is a very complex electrolyte solution, our experimental procedures would have to take the following factors into consideration:

1. When analyzing for specific ions in seawater, we are more interested in the concentration of an ion relative to the concentration of the other ions in seawater rather than the absolute concentration of the ion itself. For example, a measurement of a simple dilution of seawater is more readily made with a salinometer.
2. The standard solutions used in the preparation of the standard curve must have properties very similar to that of the unknown solution, including nearly the same ionic strength and the same significant ion interactions (ion pairs, etc.).
3. The standard solution must contain nearly the same level of interfering ions which are detected by the electrodes but which are not the ions which we are interested in measuring.

In addition, our experience showed that the equilibration time of electrodes in seawater was long and that electrode potential changed over a period of time.

With these criteria in mind, we modified the concentration calibration technique to make it more useful for seawater analysis. Our technique involves the use of commercially available artificial seawater as a seawater standard. Volumetric dilutions of the artificial seawater and the seawater solution to be analyzed (measured in units of percent concentration) are prepared. The potential of each solution is

measured with an appropriate ion specific electrode.

When doing the analysis, we alternate between unknown and standard solutions so that we first measure a potential from the 100% artificial seawater standard and then the 100% unknown and so on for the 95% and 90% dilutions. In this fashion, we generate two sets of millivolt versus concentration data for the dilution of the seawater standards and unknown seawater samples. Because of this technique, our measurements tend to be independent of experimental conditions including slope, drift, and temperature since these factors appear equally in both sets of potential versus concentration curves.

A set of parallel lines are obtained when the data are plotted on semilogarithm paper. The displacement of the unknown line from the line for the standard solution is a measure (in percent dilution) of the concentration of the ion in the unknown solution to that of a standard whose absolute value is accurately known.

If a similar set of curves for the chloride ion concentration in the artificial standard and unknown sample is prepared, it may be compared to the cation data and a determination can be made if the cation is in excess or depleted relative to its normal concentration in seawater.

We encountered experimental problems in determining electrode potentials with our electrodes because sometimes the millivolt readings rapidly changed their relative values in response to the mechanical shock of handling or to small bubbles lodged on the surface of the electrode membrane. An

electrode cell was designed which effectively eliminated these problems.



## MATERIALS AND METHODS

The Orion model 92-32 divalent cation electrode, the 92-20 calcium electrode, the 92-17 chloride electrode, and the 90-02 double junction reference electrode were prepared according to the manufacturers directions. The Fisher Accumet model 520 was used to record the electrode potential to the nearest 0.1 mv.

Artificial seawater standards were prepared using Aquarium Systems, Inc. sea salts as a standard. The composition of the seawater is given in Table 1. Reagent grade salts and deionized water were used to prepare solutions of calcium chloride, magnesium sulfate, and magnesium chloride by weight. An artificial seawater without calcium was prepared according to the formulation given in Table 2.

Figure 1 shows the electrode cell used in this study. A pyrex funnel with a diameter of 8.0 cm was fitted with a styrofoam plug 2.54 cm in thickness. The plug had suitable holes drilled in it so that the electrode could be inserted and held at the same angle as the slope of the funnel. A round plexiglas plate with a 3-mm hole drilled in the center of it was glued near the bottom of the funnel to trap and channel bubbles away from the membranes of the electrodes. An egg-shaped magnetic stirring bar was placed over the hole. A 50-ml plastic syringe was used to introduce and remove solution from the cell.

The procedure for making the measurements was as follows. The artificial seawater standards were made up by placing

TABLE 1.

Chemical Analysis, INSTANT OCEAN\* Synthetic Sea Salts (ppm).

Cl	18400	MoO <sub>4</sub>	.7
Na	10200	S <sub>2</sub> O <sub>3</sub>	.4
SO <sub>4</sub>	2500	Li	.2
Mg <sup>4</sup>	1200	Rb	.1
K	370	I	.07
Ca	370	EDTA	.05
NCO <sub>3</sub>	140	Al	.04
H <sub>3</sub> BO <sub>3</sub>	25	Zn	.02
Br	20	V	.02
Sr	8	Co	.01
SiO <sub>3</sub>	3	Fe	.01
PO <sub>4</sub>	1	Cu	.003
Mn	1		

\*Aquarium Systems, Inc.  
 33208 Lakeland Boulevard  
 Eastlake, Ohio 44094

TABLE 2.

Chemical composition of synthetic artificial seawater  
without calcium (grams/liter).

NaCl	23.476
MgCl <sub>2</sub>	4.981
Na <sub>2</sub> SO <sub>4</sub>	3.917
KCl	.664
NaHCO <sub>3</sub>	.192
KBr	.096
H <sub>3</sub> BO <sub>3</sub>	.026
NaF	.003

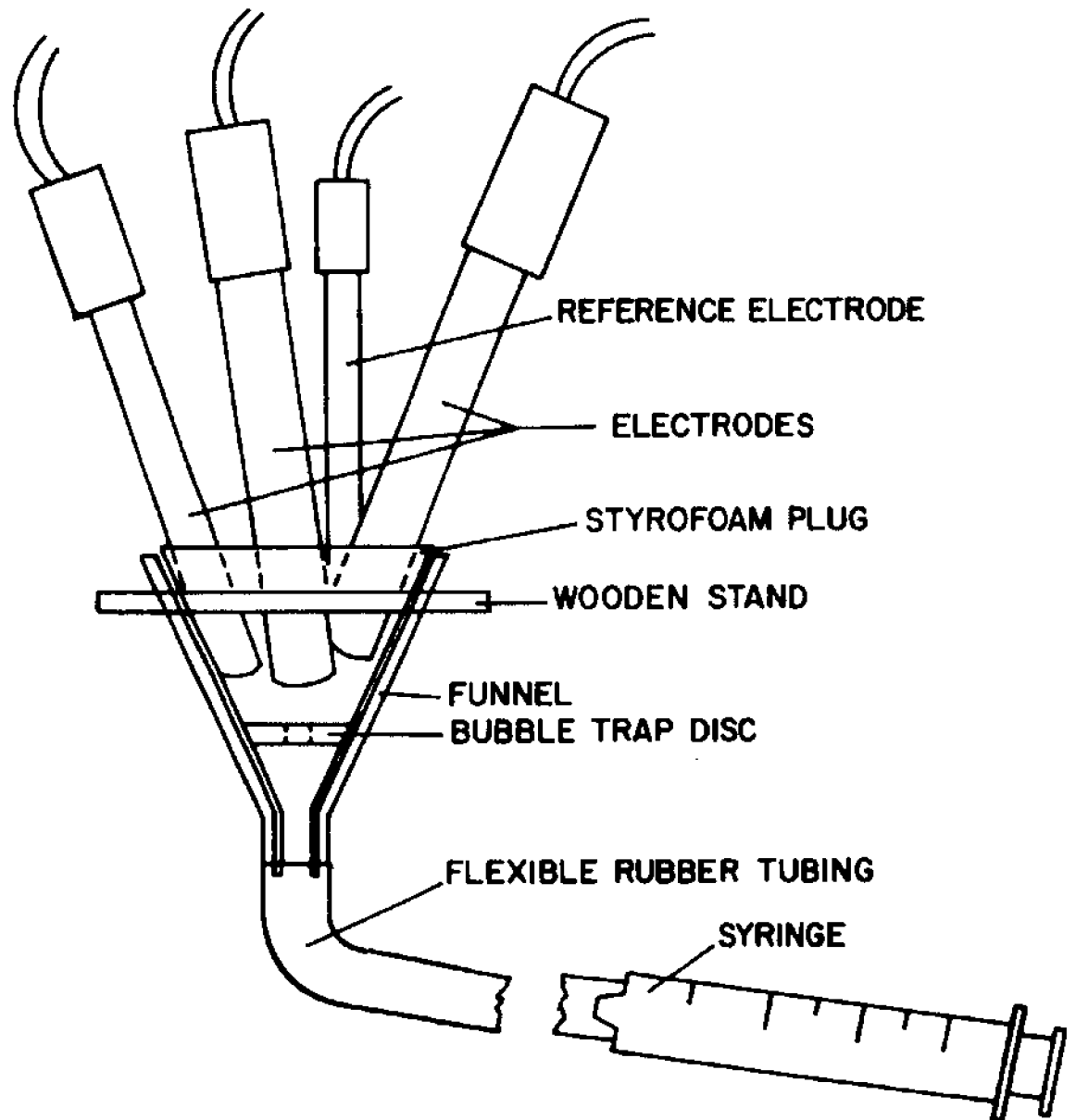


FIGURE 1 ELECTRODE CELL

100 ml, 95 ml, and 90 ml of the solution in a graduated cylinder and adding distilled water so that the final volume of all the solutions was 100 ml. A similar procedure was followed for the test solutions which were prepared by adding known volumes of calcium or magnesium solutions to a standard seawater solution.

These solutions were introduced to the cell in the sequence: 100% standard, 100% unknown, 95% standard, 95% unknown, 90% standard, and 90% unknown. Readings of the divalent calcium and chloride electrodes were recorded after introducing the solution the final time. A 50-ml plastic syringe was used for solution handling, but the cell held only about 20 ml of solution. Each solution was added to the cell and totally withdrawn using the syringe three times before a measurement was taken.

#### Data Treatment

The millivolt data from the three dilutions of the unknown solution is least squares fit to the equation:

$$mv_1 = m_1 \log c_1 + b_1, \quad (1)$$

where  $mv_1$  is the electrode potential in millivolts,  $c$  is the concentration,  $m_1$  is the slope of the line, and  $b_1$  is the intercept of the line. The correlation coefficient is calculated using the equation:

$$R = \frac{N\sum XY - (\sum X)(\sum Y)}{\sqrt{[N\sum X^2 - (\sum X)^2][N\sum Y^2 - (\sum Y)^2]}}$$

Similarly, the data for the dilution of the artificial seawater standard is also fit to equation 1. The slope and intercept data for the unknown solution are used to calculate a potential for a 100% concentration of unknown. This value of the potential is substituted into the equation which describes data for the seawater standard dilution, and the value of  $c$  is calculated. This value (in percent) represents the value of the concentration of the ion in the unknown solution relative to the seawater standard. If this procedure is repeated for both the chloride ion and the divalent ions, the relative chloride ion concentration between these two solutions can be assumed to be directly proportional to the salinity, and the percent accumulation or depletion of divalent ions in the water will be known. For example, if both the chloride concentration and divalent ion concentration relative to the standard gave a value of 110%, this means that the unknown solution is 10% more concentrated than the standard for all ions measured and the ratios are normal. If, however, the relative chloride value was 110% while the divalent value was 100% of the standard, the unknown was depleted in divalent ions by 10%.

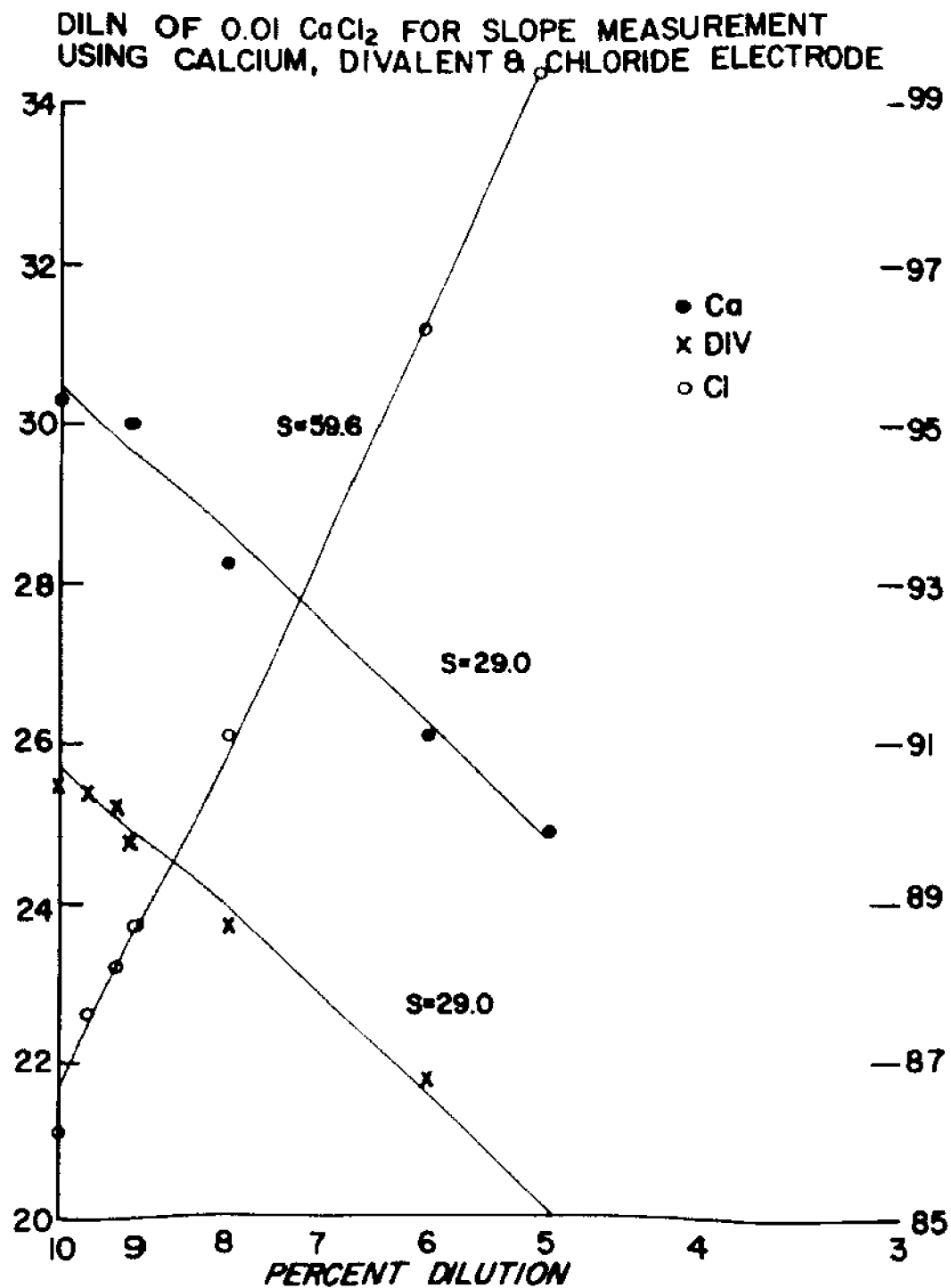
A simple computer program was written to facilitate these calculations for a large number of samples.

## RESULTS

We tested the response of the calcium, divalent, and chloride electrodes to volumetric dilutions of .01  $\text{CaCl}_2$  solution, artificial seawater, estuarine water from the Delaware Bay, and water which had been recirculated in our mariculture tanks. These data are shown in Figures 2, 3, 4, and 5. A reasonably linear plot was obtained for all of these dilutions. These seawater dilution plots, however, do not reflect the sensitivity of the electrodes to a single species since all of the ions are diluted at the same time.

In order to test the ability of the electrodes to discriminate between solutions containing depleted and excess quantities of calcium and magnesium ions relative to their normal ratios in seawater, we performed a series of experiments. Comparisons were made of the following test solutions: 1) an artificial seawater formulation without calcium and artificial seawater; 2) 5.0 ml of 0.10 M  $\text{CaCl}_2$  added to 100 ml of artificial seawater versus a standard composed of 5.0 ml of distilled water and artificial seawater; 3) a 50:50 dilution of each of the above solutions; 4) 5.0 ml of 0.10 M  $\text{MgCl}_2$  solution added to 100 ml of artificial seawater versus a standard composed of 5.0 ml of distilled water added to artificial seawater; 5) a 50:50 volumetric dilution of the unknown solution in 4); 6) .75 ml of 0.10 M  $\text{MgSO}_4$  and .75 ml of 0.10 M  $\text{CaCl}_2$  added to 100 ml of artificial seawater and a standard composed of 100 ml of artificial seawater and 1.5 ml of distilled water; and 7) a test solution of 2.5 ml of 0.10 M

FIGURE 2





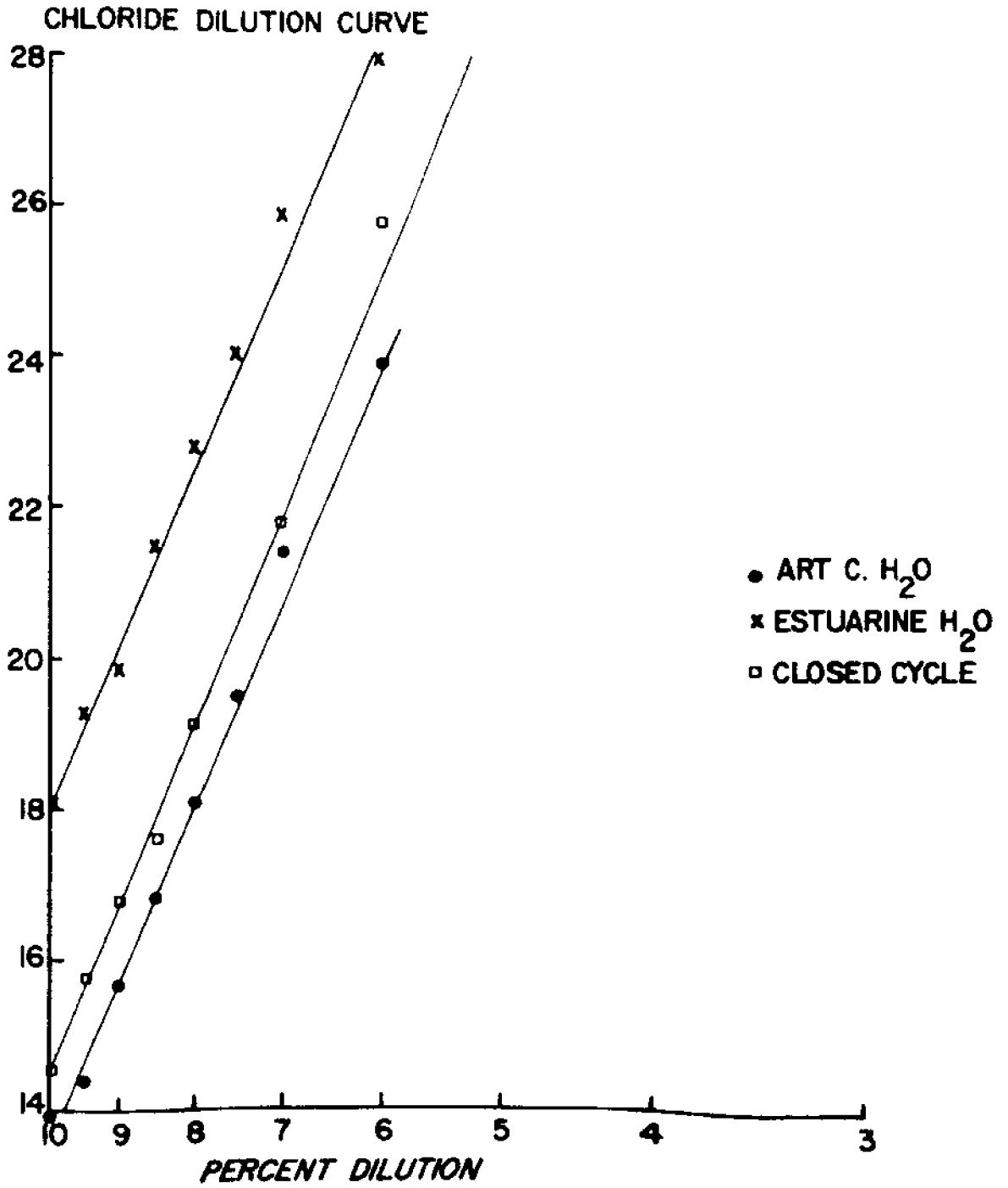


FIGURE 3

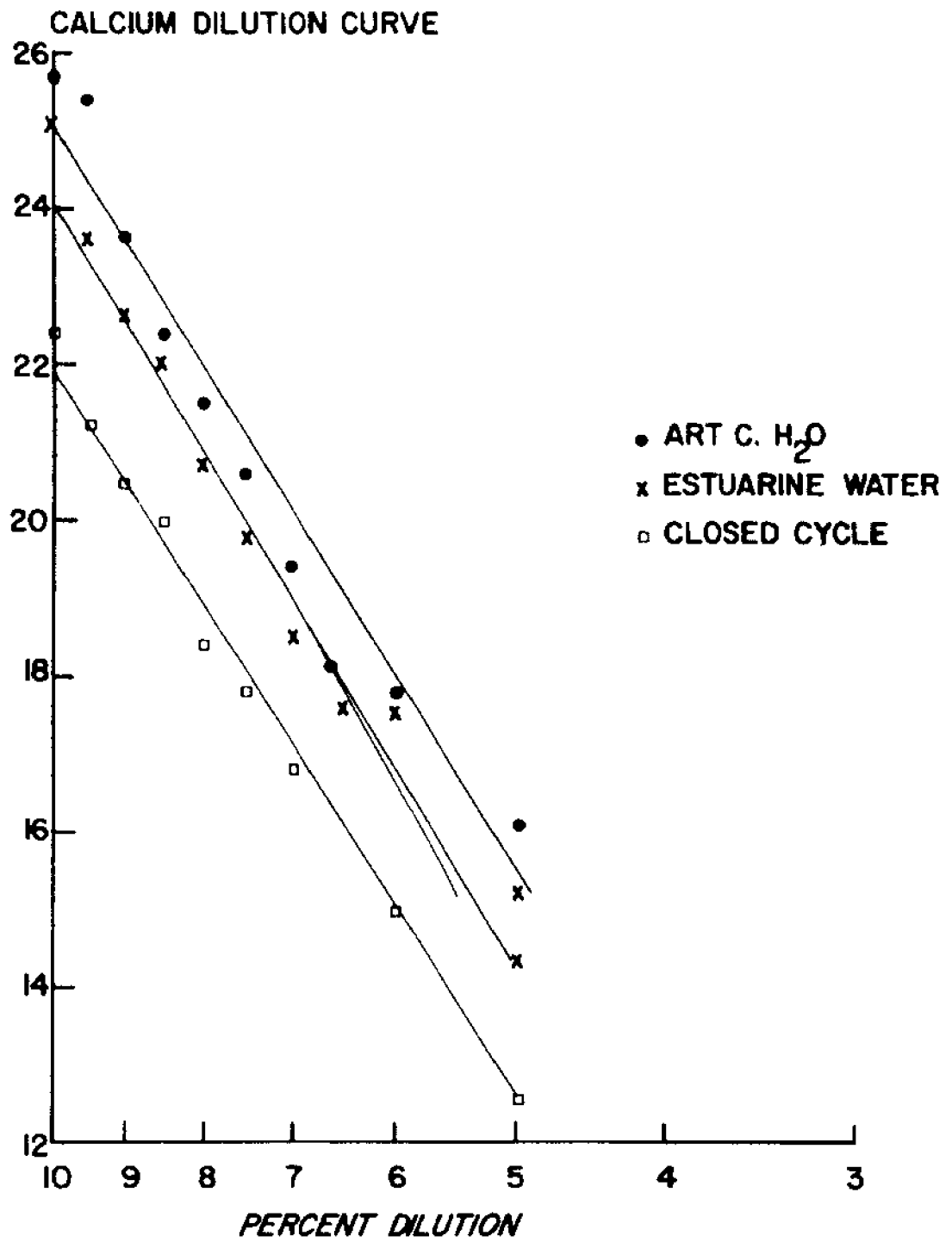


FIGURE 4

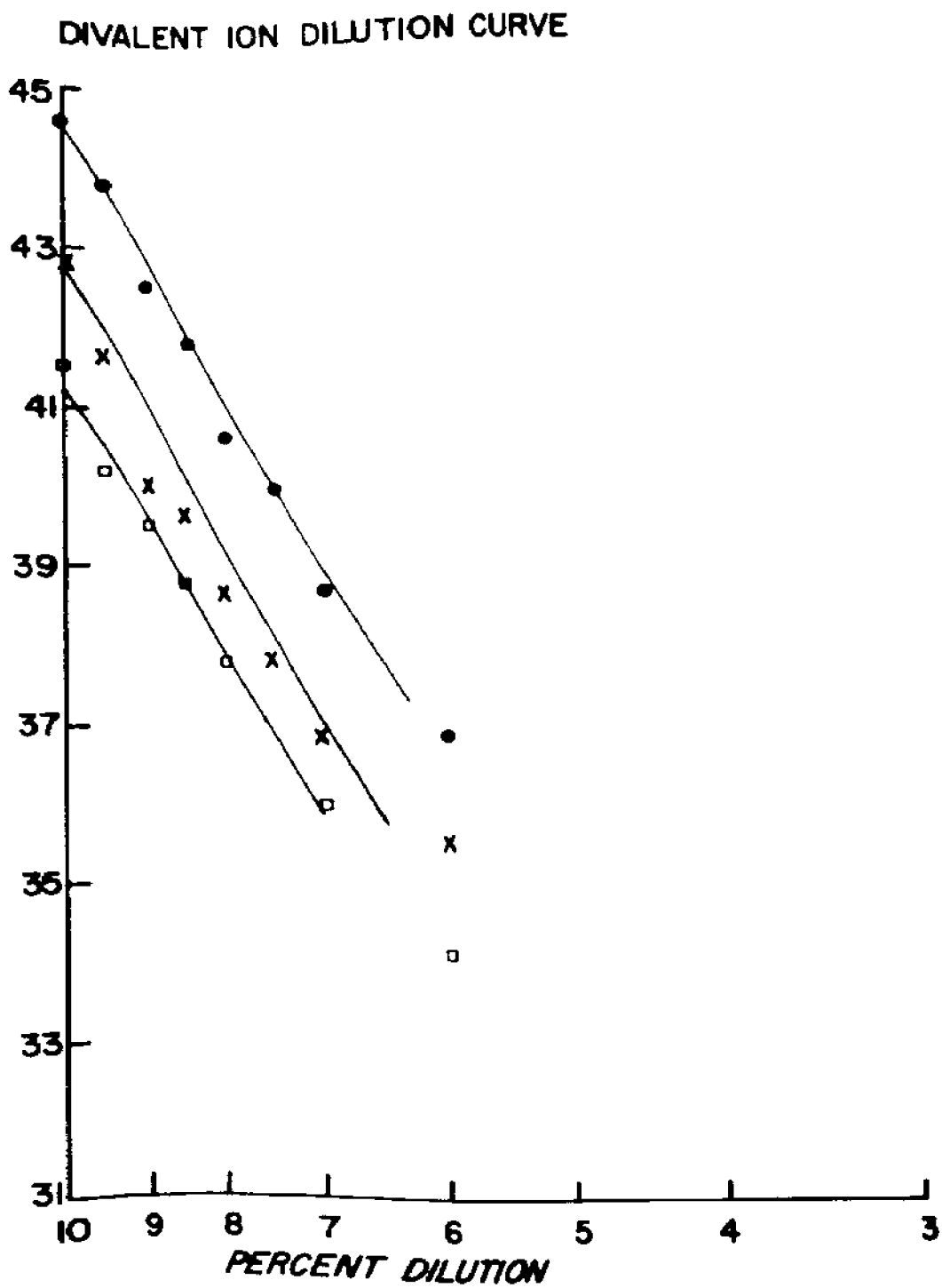


FIGURE 5

$\text{MgSO}_4$  and 2.5 ml of 0.10 M  $\text{CaCl}_2$  added to 100 ml of artificial seawater and a standard solution of 5.0 ml of distilled water added to 100 ml of artificial seawater. These solution pairs were designed to test whether the electrode technique could detect small changes in the divalent to chloride ion ratio. Table 3 shows the results of these experiments. The added solution, slope for the test and reference solution dilution curves, correlation coefficients for the dilution curve, and measured and actual relative ion accumulations are given.

The data from the calcium electrode has not been included. We found that our calcium electrode did not always give reproducible results. The electrode was returned to the manufacturer and certified to meet their specifications.

TABLE 3.

Solution 1. Artificial seawater without calcium versus an artificial seawater standard 32 ‰ salinity.

Trial	Solution	Slope	Correlation Coefficient	Measured Concentration Difference	Actual Concentration Difference
		Divalent Ion Data			
a	Unknown	19.49	.981	87%	
	Standard	19.56	.995		
b	Unknown	26.07	.997	83%	
	Standard	21.86	.953		
c	Unknown	28.23	.991	88%	
	Standard	28.20	.994		
	Average			86%	86%

TABLE 3 (continued)

Solution 2. 5.0 ml of 0.1 M  $\text{CaCl}_2$  added to  
100 ml of artificial seawater versus an  
artificial seawater standard.

Trial	Solution	Slope	Correlation Coefficient	Measured Concentration Difference	Actual Concentration Difference
Divalent Ion Data					
a	Unknown	19.56	.950	108%	
	Standard	26.00	.995		
b	Unknown	23.91	.998	107%	
	Standard	26.08	.995		
c	Unknown	45.65	.996	106%	
	Standard	34.78	.995		
	Average			107%	108%
Chloride Ion Data					
a	Unknown	-43.48	.993	104%	
	Standard	-30.43	.996		
b	Unknown	-45.65	.999	102%	
	Standard	-34.78	.997		
c	Unknown	-43.47	.991	102%	
	Standard	-36.95	.999		
	Average			102%	102%

TABLE 3 (continued)

Solution 3. Dilute both standard and solution 2, 50:50 by volume.

Trial	Solution	Slope	Correlation Coefficient	Measured Concentration Difference	Actual Concentration Difference
Divalent Ion Data					
a	Unknown	31.30	.999	108%	
	Standard	34.78	.997		
b	Unknown	30.43	.996	105%	
	Standard	30.43	.996		
c	Unknown	30.43	.987	105%	
	Standard	32.60	.999		
	Average			106%	108%
Chloride Ion Data					
a	Unknown	-63.04	.995	100%	
	Standard	-56.51	.999		
b	Unknown	-47.82	.998	101%	
	Standard	-47.82	.998		
c	Unknown	-45.65	.982	101%	
	Standard	-45.82	.994		
	Average			101%	102%

TABLE 3 (continued)

Solution 4. Add 5 ml of 0.1 M  $MgCl_2$  solution  
to 100 ml of artificial seawater.

Trial	Solution	Slope	Correlation Coefficient	Measured Concentration Difference	Actual Concentration Difference
Divalent Ion Data					
a	Unknown	28.26	.999	103%	
	Standard	26.08	1.000		
b	Unknown	28.08	.982	105%	
	Standard	26.08	.999		
c	Unknown	28.46	.999	104%	
	Standard	28.26	.976	—	
	Average			104%	108%
Chloride Ion Data					
a	Unknown	-21.74	.945	102%	
	Standard	-25.22	.970		
b	Unknown	-26.08	.960	101%	
	Standard	-23.90	.998		
c	Unknown	-26.08	.930	102%	
	Standard	-28.76	.999	—	
	Average			102%	102%



TABLE 3 (continued)

Solution 5. Dilute unknown solution 4  
50:50 volumetrically versus  
artificial seawater standard.

Trial	Solution	Slope	Correlation Coefficient	Measured Concentration Difference	Actual Concentration Difference
Divalent Ion Data					
a	Unknown	21.74	.994	52%	
	Standard	30.43	1.000		
b	Unknown	30.43	.996	58%	
	Standard	30.43	.999		
	Average			55%	54%
Chloride Ion Data					
a	Unknown	-50.60		52%	
	Standard	-44.78			
b	Unknown	-41.30		54%	
	Standard	-32.60			
	Average			53%	51%

TABLE 3 (continued)

Solution 6. 1.50 ml of 0.1 M  $\text{MgSO}_4$   
and 1.50 ml of 0.1 M  $\text{CaCl}_2$  added  
to 100 ml of artificial seawater  
versus artificial seawater standard.

Trial	Solution	Slope	Correlation Coefficient	Measured Concentration Difference	Actual Concentration Difference
Divalent Ion Data					
a	Unknown	28.26	.999	107%	
	Standard	21.73	.990		
b	Unknown	30.43	1.000	106%	
	Standard	23.90	.999		
c	Unknown	30.43	1.000	106%	
	Standard	21.70	.991		
	Average			106%	105%
Chloride Ion Data					
a	Unknown	-39.13	.998	100%	
	Standard	-34.77	1.000		
b	Unknown	-36.91	.999	101%	
	Standard	-26.08	.981		
c	Unknown	-32.60	.999	102%	
	Standard	-23.91	.987		
	Average			101%	101%

TABLE 3 (continued)

Solution 7. 2.5 ml of 0.1 M  $\text{MgSO}_4$   
and 2.50 ml of 0.1 M  $\text{CaCl}_2$  added  
to 100 ml of artificial seawater  
versus artificial seawater.

Trial	Solution	Slope	Correlation Coefficient	Measured Concentration Difference	Actual Concentration Difference
Divalent Ion Data					
a	Unknown	28.26	.999	105%	
	Standard	30.43	1.000		
b	Unknown	30.43	.999	106%	
	Standard	28.26	1.000		
c	Unknown	30.43	.999	105%	
	Standard	28.26	1.000		
	Average			105%	108%
Chloride Ion Data					
a	Unknown	-30.43	.996	101%	
	Standard	-30.43	1.000		
b	Unknown	-30.43	.996	101%	
	Standard	-30.43	.996		
c	Unknown	-30.43	.996	101%	
	Standard	-30.43	.996		
	Average			101%	101%

## CONCLUSIONS

The dilution curves given in Figures 2-5 show that a linear relationship exists between log concentration and millivolts over a range of at least a 50% dilution of seawater. This suggests that valid extrapolations can be made over a fairly wide salinity difference between the standards and the unknown solutions.

The seawater solutions containing abnormal divalent to chloride ion ratios were designed to test the ability of the electrodes to detect small changes in divalent ion to chloride ratios. The results given in Table 3 show that the slopes for the dilution curves for the standard and unknown solutions are quite similar, even though only three data points were used and the potential differences measured were very close to the limits of detection of the electrode method (Whitfield, 1971). The data are accurate to better than  $\pm 2\%$ .

The method and apparatus effectively eliminated problems due to electrode drift, electrode shift, and temperature equilibrium which often reduce the accuracy of electrode measurements. We made no special attempt to fix the temperature of the solutions and used equilibration times of less than 15 seconds. Bubbles did not adhere to the electrode membranes, and the electrodes were not subjected to mechanical shock.

The procedure employed utilizes artificial seawater dilutions as reference standards. This is realistic since both calcium and magnesium ions have strong interactions with other

ions in seawater (Garrels and Thompson, 1962), and thus the activity of these ions differs considerably from that of pure solutions at the same concentration.

For each analysis, three measurements of the unknown solution are made rather than the one measurement usually made in concentration calibration techniques. Concurrent chloride ion measurements allow the data to be used to distinguish between a simple dilution of seawater and a solution containing different ratios of seawater ions.

Our inability to incorporate direct calcium ion measurements into our technique is a limitation of the technique since calcium comprises only 15% of the total divalent ion concentration. Thus, a depletion of this ion alone in seawater is relatively difficult to detect when just the divalent ion specific electrode is employed. Thompson and Ross (1966) reported quite accurate measurements of calcium in seawater using this electrode, so it may be possible to overcome the experimental difficulties which we experienced.

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