

ALKALINITY DETERMINATION IN HYPERSALINE SOLUTIONS: A METHOD FOR OVERCOMING GLASS ELECTRODE ERRORS

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ABSTRACT

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The non-ideality of commercially available glass pH electrode normally used for alkalinity determination by the Gran-type titration has been examined and its effect on the accuracy of the estimated alkalinity evaluated. It is found that slope errors of the glass electrode could be a limiting factor to the accuracy that can be obtained. This error source could be eliminated altogether by applying the proposed 'slope correction' algorithm which uses the titration data for in situ slope calibration of the glass electrode. Application of the proposed method eliminates the need for calibration of the glass electrode and the requirement for thermostating the test solution.

INTRODUCTION

Alkalinity is often chosen as a master variable when characterizing natural, industrial and aquaculture solutions because it is linked to the processes which control pH buffering but yet it is a conservative parameter (i.e. temperature and pressure independent) and relatively easy to determine with high accuracies (Edmond, 1970; Johnson et al., 1977; Johansson, 1981; Dickson, 1981; Pearson, 1981). Among the possible analytical methods for alkalinity determination, Gran-type potentiometric titration (Gran, 1952) combined with a curve-fitting algorithm is considered a suitable method for alkalinity determination in hypersaline solutions (Sass and Ben-Yaakov, 1977) because it does not require a priori knowledge of thermodynamic parameters such as activity coefficients and dissociation constants which must be known when other analytical methods for alkalinity determination are applied (Culberson et al., 1970; Pearson, 1981; Dickson, 1981).

Alkalinity determination in hypersaline solutions by the Gran-type titration is subject to a number of errors which can usually be neglected in lower ionic strength solutions. For example, the pH readings along the titration path may be inaccurate due to the marked difference between the

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ionic strength and composition of the tested brine and the standard buffers used to calibrate the glass and reference electrode pair (Bates, 1964). The purpose of this study was to identify the possible error sources encountered during an alkalinity determination in brines by a Gran-type titration and to analyze the possible effects of these errors on the accuracy of the measured alkalinity. Special attention was paid to errors due to possible non-ideal behavior of glass-reference electrode pair in brine. The conclusions of the theoretical error analysis were then used to develop a titration procedure and an associated algorithm which may simplify alkalinity determination in hypersaline and other solutions by overcoming problems due to non-ideal behavior and instability of commercial pH electrodes.

The alkalinity estimation method as presented earlier (Sass and Ben-Yaakov, 1977) was used as the basic procedure in the present work. The method is based on the assumption that for the region past the equivalence point, where the concentration of bicarbonate and carbonate ions can be neglected, the titration data can be presented by a linear relationship of the form

$$a_{\text{H}}(V_0 + V_a) = A_0 V_0 \gamma_{\text{H}} + N_a \gamma_{\text{H}} V_a \quad (1)$$

where A_0 = original total alkalinity, N_a = normality of titrating acid, V_0 = initial sample volume, V_a = accumulative volume of added titrant, a_{H} = hydrogen ion activity, γ_{H} = proton single ion activity coefficient.

It is assumed that for the solutions under consideration, the alkalinity contributions of protolytic species having an equivalence point past (at a lower pH region) the equivalence points of the main species (bicarbonate) is negligibly small (Edmond, 1970; Culberson et al., 1970; Mehrbach et al., 1973; Johansson, 1981).

The more refined approaches which take into account second-order effects, such as the contribution of the residual bicarbonate ion, usually cannot be used in hypersaline solutions because the required data on the association constants is unavailable (Dickson, 1981) Application of non-linear curve fitting methods to extract the unknown parameters was deemed superfluous for alkalinity determination in brines which usually exhibit high degree of variability both in terms of ionic composition and ionic strength. It was found that the accuracy of the estimated alkalinity by the proposed algorithm is acceptable in many applications even though the effect of protonation of species such as sulfate, phosphate and fluoride (Johansson, 1981; Dickson, 1981) is neglected here.

ERROR ANALYSIS

a_{H} required for estimating alkalinity by eq. 1 is calculated from pH which is normally determined by a glass and reference electrode calibrated against standard buffer solutions (Bates, 1964). The calibration curve is of

the form (Bates, 1964):

$$\text{pH} = S \cdot E + B \quad (2)$$

where E = glass-reference electrode pair output voltage, S = slope of glass-reference electrode (ideally Nernst slope), B = offset voltage (around pH 7 for most commercial glass electrodes in which an internal pH 7 buffer solution is used). It should be noted that B includes the errors due to the difference in the liquid junction potentials between the standardizing buffers and tested brine.

Examination of eq. 2 reveals that the pH electrode pair could introduce error in a_{H} due to inaccuracy in the assumed slope S and offset B , needed to derive pH from the actually measured parameter E (as measured directly or via a standard pH meter) along the titration curve. It can easily be shown that the net effect of an error ΔB in the slope will result in an erroneous value for γ_{H} (γ'_{H})

$$\gamma'_{\text{H}} = \gamma_{\text{H}} 10^{\Delta B} \quad (3)$$

However, since the calculated alkalinity will be unaffected, one can conclude that this method of alkalinity determination is independent of offset errors of the glass-reference electrode pair.

The effect of an error in S (eq. 2) is now evaluated by assuming a constant error ΔS in the electrode slope. The calculated (erroneous) a'_{H} will thus be

$$a'_{\text{H}_i} = a_{\text{H}_i} \times 10^{-\Delta S E_i} = (a_{\text{H}_i})^{(1 + \Delta S/S)} \times 10^{-(\Delta S \cdot B)/S} \quad (4)$$

Hence, a constant slope error, ΔS , causes two simultaneous errors. The first is a multiplying-factor error ($10^{-\Delta S \cdot B/S}$), having the same effect as an offset error and therefore not affecting alkalinity estimation. The second is a power error in a_{H} , which introduces a non-linearity to the measured data. The non-linearity causes the data to deviate from a straight line and the extrapolated alkalinity will thus be in error.

SUGGESTED SLOPE CORRECTION ALGORITHM

In order to amend the non-linearity introduced to the a_{H} values due to the slope error, all a'_{H} values should be raised to the power of $1/(1 + (\Delta S/S))$, this value will be denoted by SC and called the 'slope correction' factor. Raising a'_{H} (eq. 4) to the power of SC yields

$$a'_{\text{H}} = a_{\text{H}} \times 10^{-(\Delta S \cdot B/S)SC} \quad (4a)$$

leaving only the multiplying factor error which, as previously shown, does not affect alkalinity estimation. Since the value of ΔS is unknown, trial and error iterations on SC must be carried out. The right value of SC to be finally chosen is the one that gives the minimum deviation of the amended data from a linear regression line, i.e., the best statistical correlation coefficient. SC can assume values bigger or smaller than one, depending on the sign of ΔS . It should be emphasized that there is no need for a priori knowledge of

the pH electrode slope when applying the suggested iterative algorithm. The only requirement is that the response of the electrode shall follow the relationship of eq. 2 along the region of interest, i.e. the range of pH used for the modified Gran titration procedure. The iteration sequence could be started by assigning any arbitrary value S' to the slope for which the best slope correction factor SC is selected by the algorithm. The true slope of the electrode is then $S' \cdot SC$. Hence, this procedure represents, in fact, an independent method for slope calibration of a glass electrode by mathematical manipulation of the same titration data which is then used for alkalinity determination.

EXPERIMENTAL

Simulation

Simulation of the slope correction procedure theory outlined above was carried out on a synthetic set of data points, to which a pseudo-random distributed noise was later added. Synthetic data sets were obtained from eq. 1 assuming $A = 2.69 \mu\text{eq cm}^{-3}$, $\gamma_{\text{H}} = 0.6$, $V_0 = 250 \text{ cm}^3$, $N_a = 0.5 \text{ N}$ and $\Delta V_a = 0.1 \text{ cm}^3$. The first value of V_a past the equivalence point was chosen to be 1.4 cm^3 . a_{H} values were calculated for each value past the initial V_a value, and up to 2.5 cm^3 . The simulation was carried out on a CBM type 3032 (Commodore Business Machines, U.S.A.) microcomputer, to which a CBM 2040 dual diskette drive and a Tektronix (U.S.A.) type 4662 plotter were interfaced. A standard least square fitting method (Bevington, 1969) was used to realize the suggested algorithm.

Titration assembly

The titration assembly was similar to the one described by Ben-Yaakov et al. (1982). All titrations were carried out at room temperature which was in the range of 23°C to 28°C .

Electrode. pH was measured by a Broadley James Corp. (U.S.A.) type 9006 pH electrode.

Reagents. All reagents used were analytical grade. Titrating solution was 0.1 N HCl. Aristar standard (BDH Chemicals). pH 7 and pH 4 buffers were Titrisol Standard (Merck).

Solutions. Titrations were carried out on synthetic Dead Sea Brine (approximate salinity of 287 g kg^{-1}) and Mediterranean Sea water (approximate salinity of 41 g kg^{-1}). Salinities and compositions of the synthetic solutions were according to Amit and Bentor (1971), except that sulfate in the Dead Sea water brine and in one sample of synthetic Mediterranean Sea water was replaced by chloride.

Titration procedure. Repeated titrations were carried out on the same synthetic solution batches on 100 cm^3 samples which were titrated with 3 to 5 cm^3 of titrating acid, i.e. 30–50 burette increments. pH 7 and pH 4 buffers were used for initial calibration of the pH combination electrode.

RESULTS AND DISCUSSION

The suggested iterative procedure was tested on the synthetically generated data. Data corruption due to slope error was simulated by arbitrarily raising the a_{H_i} values to the power of $1/0.96$. Hence the iteration procedure should have converged to value of 0.96 for the slope correction (SC) factor. The improvement in R^2 as SC was incremented was found to be rather dramatic for these noise-free synthetic data. A 0.01 deviation of SC factor from the correct value (0.96) caused a drop in R^2 from 0.99999999 to about 0.999992 which can easily be detected by the inherent resolution (9 significant figures) of the microcomputer used. The extremely high correlation ($R^2 \simeq 1$) found here suggests that the proposed algorithm is effective in extracting the SC value to much better than 0.01 units for noise-free data. The almost perfect fit that is obtained restores the data to the expected linear relationship (eq. 2), even though the deviation can hardly be seen by examination of the original Gran plot. The expected error in the estimated alkalinity from the titration data is found here to be about 0.01 meq l^{-1} per 0.01 error in the slope. That is, a 1% error in the assumed value of the glass-electrode slope will cause about 0.5% error in seawater alkalinity if a slope correction algorithm is not used.

The effects of data noise on the suggested algorithm were examined under the assumption that the noise of the measured pH values is significantly larger than all other noise sources. This was deemed to be a reasonable assumption considering the fact that standard laboratory techniques could reduce errors in V_a , N_a and V_0 (eq. 1) to well below 0.1% whereas 0.01 pH unit error corresponds to about 2.3% error in a_{H} .

The noise-corrupted data was simulated by adding a Gaussian-distributed pseudo-random noise with zero mean to the synthetic data. Since the assumed slope of the glass electrode was not perturbed from the theoretical value, in this set of calculations, the normal regression procedure (Sass and Ben-Yaakov, 1977) and the slope correction algorithm produces the same alkalinity value for noise-free data (Table I). In this case the SC algorithm converged to the value $SC = 1$ as expected. However, as the noise was increased from $\sigma = 0.1$ pH units to $\sigma = 0.4$ pH units (corresponding to 6 and 24 mV noise at 25°C), the improvement in alkalinity estimation by the slope correction algorithm became more and more significant (Table I). It is thus apparent that although the algorithm was originally intended for correcting slope error, it is also effective in selecting a better fit to data with randomly distributed pH noise. This could be explained by examining the nature of a_{H} noise that will result from a randomly distributed pH perturbation. The noise-corrupted a_{H} is related to pH and associated error E_{pH} by

$$a'_{\text{H}} = 10^{-(\text{pH} + E_{\text{pH}})} = a_{\text{H}} \times 10^{-E_{\text{pH}}} \quad (5)$$

The magnitude of the noise is therefore

$$E_{a_{\text{H}}} = a_{\text{H}} \times 10^{-E_{\text{pH}}} - a_{\text{H}} = a_{\text{H}}(10^{-E_{\text{pH}}} - 1) \quad (6)$$

TABLE I
Effect of pH data noise on calculated alkalinity by conventional and modified Gran plot

pH units	Added noise (σ)	Without slope correction ($SC = 1$)				With slope correction				
		mV	R^2	γ_H	$A \times 10^{-3}$	$\Delta A \times 10^{-3}$	R^2	γ_H	$A \times 10^{-3}$	$\Delta A \times 10^{-3}$
0	0	1	0.6	2.690	0	1	0.6	2.690	0	1
0.1	6	0.9981	0.592	2.683	0.007	0.9982	0.519	2.697	0.007	1.02
0.2	12	0.9931	0.481	2.671	0.019	0.9949	0.445	2.698	0.008	1.04
0.3	24	0.9585	1.182	2.609	0.081	0.9642	0.394	2.706	0.016	1.06

which implies that the magnitude of E_{a_H} is increasing as the pH becomes more acidic (a_H is getting larger). The range of the error is $a_H |10^{|\text{pH}|} - 1|$ to $a_H |1 - 10^{-|\text{pH}|}|$ which is unequally distributed around a_H because

$$(10^{|\text{pH}|} - 1) > (1 - 10^{-|\text{pH}|}) \quad (7)$$

This curvature is fitted by the non-linear transformation $(a_H)^{SC}$ of the slope correction algorithm improving, thereby, the conformity to linear relationship.

The ability of the suggested slope correction algorithm to linearize curved a_H data, will also affect curvature due to other effects. For example, protonization of species such as sulfate and phosphate over the pH range of interest, will result in a deviation of the Gran plot from the straight line of eqs. 1 and 2 (Mehrbach et al., 1973; Johansson, 1981; Dickson, 1981). If some ions x_j^- are reacting appreciably with the hydronium ion over the relevant pH range, i.e.



eq. 1 must be amended to the form

$$\left(a_{H_i} + \sum_{j=1}^n \frac{Tx_j}{1 + (Kx_j/a_{H_i})} \right) \times (V_0 + V_{a_i}) = AV_0\gamma_H + N_a\gamma_H V_{a_i} \quad (9)$$

where Kx_j is the apparent dissociation constant of the j th species, and Tx_j is the total concentration of x_j ($|x_j^-| + |Hx_j|$). When the slope correction algorithm is operated on such data it attempts to linearize it by substituting the numerical value of $(a_{H_i})^{SC}$ for

$$a_{H_i} + \sum_{j=1}^n \frac{Tx_j}{1 + (Kx_j/a_{H_i})}$$

which has the net effect of reducing the curvature of the data. This effect was studied by processing the synthetic data of alkalinity titration presented by Dickson (1981). The data are based on a seawater model which includes a 10^{-5} mol kg $^{-1}$ phosphate solution, 7×10^{-5} mol kg $^{-1}$ solution fluoride and 28.24×10^{-3} mol kg $^{-1}$ solution of sulfate. It was found that an apparent linear relationship ($R^2 = 0.999993$) is restored when a SC of 0.96 is used, i.e. when the a_{H_i} values are replaced by $(a_{H_i})^{SC}$. The implication of this non-linear transformation to the accuracy of the computed alkalinity is obviously non-trivial. The results of the present study suggest, however, that it does not affect the accuracy of alkalinity determination in seawater and Dead Sea water by the proposed method.

Application of the proposed algorithm to experimentally derived titration data reveals that the procedure can effectively select the slope for best linear

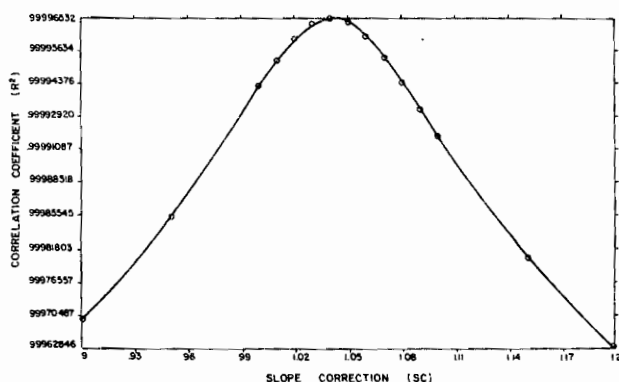


Fig. 1. Regression correlation as a function of SC values for experimental titration data solution: synthetic Dead Sea brine of 2 meq l^{-1} alkalinity (No. 2 in Table II).

correlation (Figs. 1 and 2). However, the sensitivity of the correlation coefficient which is used as a fitting criterion to the slope correction factor is lower in this case than the one found for synthetic titration data. That is, the peak of the $R^2 = f(SC)$ (Fig. 1) function of real data is much broader than the simulated one. This effect is a manifestation of the non-ideality of the titration data, which are subject to errors due to: instrumentation noise, non-ideal response of the glass electrode and possibly unaccounted for proton reaction over the pH range of interest. Maximum correlation was found in this case for a slope correction factor of 1.03. This implies that the assumed glass-electrode slope was too low by about 4% from the slope that produced the best linear correlation. The small difference is indicative of the fact that the electrodes had been calibrated prior to the titration. If the

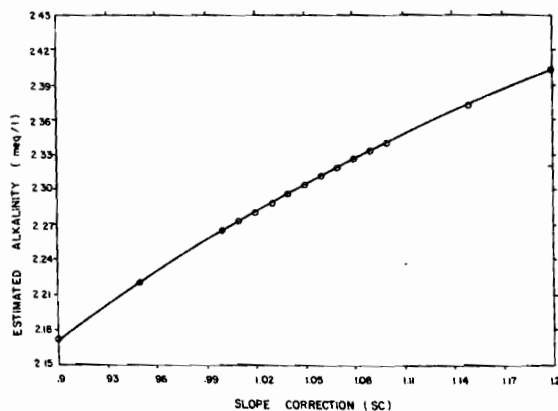


Fig. 2. Regression errors for experimental titration data (same as in Fig. 1) without slope correction ($SC = 1$) and with optimally corrected slope ($SC = 1.04$).

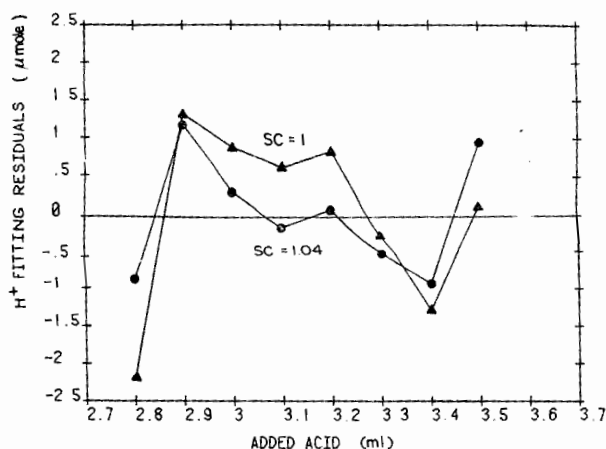


Fig. 3. Computed alkalinity as a function of SC for experimental titration data. Solution: synthetic Dead Sea brine of 2 meq l^{-1} alkalinity (No. 2 in Table II).

electrode could not have been calibrated, the iteration procedure could have been started with any arbitrary assigned slope for which the suitable SC would have been selected. In both cases, the estimated alkalinity will be the same since it corresponds to the one calculated for maximum correlation irrespective of the numerical value of SC . In this specific case the estimated alkalinity is chosen as the one corresponding to the $SC = 1.04$ (Fig. 3). It should be noted that the alkalinity estimate is rather sensitive to SC as a SC deviation of 0.01 corresponds to an uncertainty of 0.007 meq l^{-1} or about 0.3% for the case under study.

The accuracy of the proposed method was tested experimentally by running duplicate titrations on distilled water, artificial seawater with and without sulfate and artificial Dead Sea waters (Table II). For each run, alkalinity was calculated by two methods: (a) by the conventional Gran plot which preassumes that the glass electrode is properly calibrated and (b) by the proposed method which applies the titration data for in situ calibration of the glass electrode by the slope correction algorithm. The precision of the proposed method when applied in the distilled water runs was found to be significantly better than the conventional method. This should be attributed to the non-stability of the glass electrode which is corrected for by the proposed algorithm. It is also interesting to note that the average alkalinity as determined by the proposed method is higher by about 0.04 meq l^{-1} compared to the average value obtained by the conventional method. This 2% error is much larger than the expected uncertainty in the alkalinity of the test solution. The discrepancy could be due to temperature instability which may cause appreciable errors if the slope correction algorithm is not used. The average alkalinity value obtained from the iteration processes

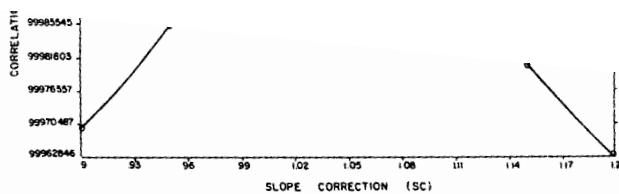


Fig. 1. Regression correlation as a function of SC values for experimental titration data solution: synthetic Dead Sea brine of 2 meq l^{-1} alkalinity (No. 2 in Table II).

correlation (Figs. 1 and 2). However, the sensitivity of the correlation coefficient which is used as a fitting criterion to the slope correction factor is lower in this case than the one found for synthetic titration data. That is, the peak of the $R^2 = f(SC)$ (Fig. 1) function of real data is much broader than the simulated one. This effect is a manifestation of the non-ideality of the titration data, which are subject to errors due to: instrumentation noise, non-ideal response of the glass electrode and possibly unaccounted for proton reaction over the pH range of interest. Maximum correlation was found in this case for a slope correction factor of 1.03. This implies that the assumed glass-electrode slope was too low by about 4% from the slope that produced the best linear correlation. The small difference is indicative of the fact that the electrodes had been calibrated prior to the titration. If the

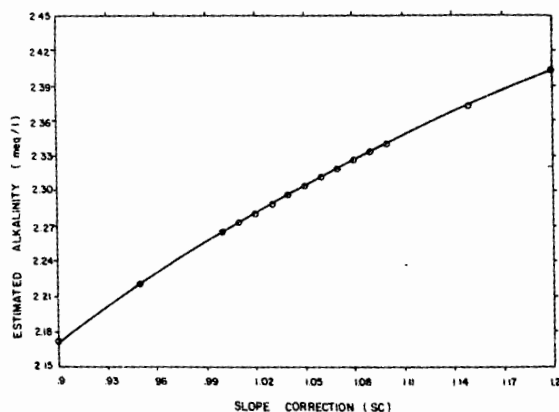


Fig. 2. Regression errors for experimental titration data (same as in Fig. 1) without slope correction ($SC = 1$) and with optimally corrected slope ($SC = 1.04$).

TABLE II
Computed alkalinities from experimental titr

Water Type	Disilled water		Synthetic Mediterranean Sea wa		Nr.	
	Added alkalinity 2 meq l^{-1}	SC	Yes	No		
2,1	1.986	2.003	2.003	0.0347	0.0311	2,1
	1.929	2.000	2.000	0.0289	0.0428	2,1
	1.914	2.000	2.000	0.0282	0.0539	2,1
	2.016	2.008	2.008	7.62×10^{-5}	0.0391	2,1
	1.989	2.006	2.006	0.0346	0.0439	2,1
	1.926	2.001	2.001	0.0233	0.0491	2,1
	2.004	2.004	2.004	0.0108	0.0398	2,1
	1.929	2.002	2.002	0.0239	0.0284	2,1
	1.981	2.007	2.007	0.0380	0.0687	2,1
Average alkalinity	1.968	2.0036	0.02449	0.0438	2.0	
Alk. std. deviation	1.29×10^{-3}	9.27×10^{-4}	4.07×10^{-4}	4.17×10^{-3}	6.1	

(2.0036 meq l⁻¹) is within 0.2% of the expected value (2.00 meq l⁻¹). This deviation, however, is well within the estimated error of the standard solutions used. Using the $\pm 2\sigma$ as a measure of the precision, the precision of the proposed method ($\pm 0.1\%$) is also in reasonable agreement with the expected experimental uncertainty of the present study. On the other hand, the precision of the conventional method ($\pm 1.3\%$) is markedly inferior to the analytical precision. This large uncertainty is most likely linked to temperature variation which is overcome by the proposed slope correction algorithm. For solutions other than distilled water, the improvement of the proposed method over the conventional method, which assumes well-calibrated electrodes, was found to be insignificant if the glass electrodes are meticulously calibrated prior to each run (Table II). Consequently, one can conclude that commercial glass electrodes retain their slope (i.e. $\Delta E/\Delta \text{pH}$) in Dead Sea brine. In this respect, the proposed slope correction algorithm does not improve the accuracy of alkalinity determination in hypersaline solutions. The advantage of the algorithm is thus mainly operative: it eliminates the need for calibration of the glass electrode and the requirement for thermostating the standard and test solution.

The results of the present study suggest that the uncertainty in alkalinity determination in Dead Sea brine by the Gran titration is about $\pm 2\%$ (two sigmas) compared with about $\pm 0.1\%$ in distilled water (Table II). It appears that the high ionic strength and unaccounted for proton reactions cause a deviation of the titration data from the sample titration model (eq. 1) used here. This could possibly be improved by refinement of the titration model when more data on proton reactions in hypersaline solutions are available.

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REFERENCES

- Amit, O. and Bentor, Y.K., 1971. pH—dilution curves of saline waters. *Chem. Geol.*, 7: 307—313.
- Bates, R.G., 1964. *Determination of pH — theory and practice*. Wiley, New York, 435 pp.
- Ben-Yaakov, S., Raviv, R., Guterman, H., Dayan, A. and Lazar, B., 1982. Application of personal computers in the analytical laboratory. I. Potentiometric analysis. *Talanta*, 29: 267—274.
- Bevington, P.R., 1969. *Data Reduction and Error Analysis for the Physical Sciences*. McGraw-Hill, New York, 336 pp.
- Culberson, C., Pytkowicz, R.M. and Hawley, J.E., 1970. Seawater Alkalinity Determination by the pH method. *J. Mar. Res.*, 28: 15—21.
- Dickson, A.G., 1981. An exact definition of total alkalinity and a procedure for the estimation of alkalinity and total inorganic carbon from titration data. *Deep-Sea Res.*, 28A: 609—623.

- Edmond, J.M., 1970. High precision determination of titration alkalinity and total carbon dioxide content of sea water by potentiometric titration. *Deep-Sea Res.*, 17: 737-750.
- Gran, G., 1952. Determination of the equivalence point in potentiometric titrations. Part II. *Analyst*, 77: 661-671.
- Johnson, K.S., Voll, R., Curtis, C.A. and Pytkowicz, R.M., 1977. A critical examination of the NBS pH scale and the determination of titration alkalinity. *Deep-Sea Res.*, 24: 915-926.
- Johansson, O., 1981. Protolytic equilibria in sea water. Thesis, University of Gothenburg.
- Lyman, J., 1956. Buffer mechanism of sea water. Ph.D. Thesis, University of California, Los Angeles, 196 pp.
- Mehrbach, C., Culberson, C.H., Hawley, J.E. and Pytkowicz, R.M., 1973. Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. *Limnol. Oceanogr.*, 18: 897-907.
- Pearson, F., 1981. Fixed endpoint alkalinity determination. *J. Water Pollut. Control*, 53: 1243-1252.
- Sass, E. and Ben-Yaakov, S., 1977. The carbonate system in hypersaline solutions: Dead Sea brines. *Mar. Chem.*, 5: 183-199.