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Measurement of Fluoride Activity and Concentration in Seawater Using a Lanthanum Fluoride Electrode

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ABSTRACT

Fluoride ion activity is quickly and easily determined in seawater, using a fluoride-selective electrode. Samples require little pretreatment, a determination takes 15 minutes, demands made on the operator are minimal, and the equipment required is rugged, inexpensive, and motion insensitive. The ratio of fluoride activity to total fluoride concentration is given as a function of salinity at constant temperature; where normal ion ratios are encountered, the total concentration may be determined to ±5% using the shipboard method described. The method lends itself to adaptation for *in situ* analysis.

PROBLEM STATUS

This is an interim report; work on this problem is continuing.

AUTHORIZATION

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MEASUREMENT OF FLUORIDE ACTIVITY AND CONCENTRATION IN SEAWATER USING A LANTHANUM FLUORIDE ELECTRODE

INTRODUCTION

Specific ion electrodes offer an attractive approach to the analysis of minor constituents in complex solutions (1). They are particularly suited to the examination of ionic equilibria, since they respond to free ion activity rather than total concentration. When the composition of the test solution is sufficiently defined, they may also be used for analysis of the total concentration. The determination of fluoride in seawater is a representative problem of particular interest, because fluoride may not be a conservative constituent (2). The most precise method available, that of Greenhalgh and Riley (3), determines fluoride spectrophotometrically as the lanthanum alizarin complexone complex in aqueous acetone solution. These authors give a good critical review of other methods. Recently Wilkniss and Linnenbom (4) described a new method based on photon activation analysis that was free from interferences due to complexation of fluoride and offered promise of determining all the halides simultaneously. Neither of these methods appears easily adaptable to in situ measurement.

The LaF_3 electrode recently introduced by Frant and Ross (5) responds selectively to fluoride in the presence of many other ions. High chloride ion concentrations do not degrade response, even at ion ratios greater than 10^6:1 (6,7). Because its output is a stable and accurately predictable voltage, it should be adaptable to direct in situ measurements. Its utility for the shipboard analysis of fluoride in seawater is examined here, and a simple method is described. Results are given for measurements in (a) synthetic seawaters of constant total ionic strength μ and variable fluoride concentration, (b) seawater with variable μ and known relative fluoride concentration, (c) seawater containing known additions of fluoride, and (d) in seawater whose fluoride content was also determined by an independent method. A preliminary report has been made elsewhere (8).

THEORETICAL CONSIDERATIONS

The fluoride electrode consists of an inner reference electrode separated from the test solution by a single-crystal membrane of LaF_3, which is essentially only permeable to fluoride ions. The only significant interference is from the hydroxide ion; such interference is negligible when hydroxide activity is less than one-tenth that of fluoride (5). Under isothermal conditions, the electrode potential E versus a suitable reference electrode is accurately given by the Nernst equation,

$$E = \text{[illegible]} - \frac{RT}{F} \ln a, \tag{1}$$

where a is the fluoride ion activity and R, T, and F are the gas constant, absolute temperature, and faraday, respectively. The value of [illegible] depends on the choice of inner and outer reference electrodes and on the composition of the inner reference solution as well as any liquid junction potentials within the cell. If the standard and test solutions are very similar, liquid junction potential changes are kept small, [illegible] remains virtually constant, and the activity may be directly determined in the presence of large excesses of other ions.

Relation Between Activity, Concentration, and Salinity–General Case

In seawater, where the standard and unknown will, in general, be solutions of different salinity and hence of different ionic composition, it is necessary to know the relation between fluoride activity and fluoride total concentration in different waters. In this report we restrict ourselves to fluoride present in the inorganic form, and total concentration always means total inorganic fluoride.

Fluoride ion activity is related to free uncomplexed fluoride ion concentration $[F^-]$ and the fluoride ion activity coefficient γ via the relation

$$[F^-] = \frac{a}{\gamma}. \tag{2}$$

In seawater, part of the total fluoride concentration C is tied up in the MgF^+ complex via the equilibrium

$$Mg^{++} + F^- \rightleftarrows MgF^+ \tag{3}$$

with the concentration formation constant

$$K_c = \frac{[MgF^+]}{[Mg^{++}][F^-]}, \tag{4}$$

where $[Mg^{++}]$ is the concentration in gram-atoms/liter of Mg^{++} not tied up in other complexes. Since the MgF_2 complex binds negligible amounts of fluoride in the sea, the total concentration of fluoride is

$$C = [MgF^+] + [F^-] = [F^-](K_c[Mg^{++}] + 1). \tag{5}$$

Hence, C is related to a via

$$C = a\left(\frac{K_c[Mg^{++}] + 1}{\gamma}\right). \tag{6}$$

Assume that the concept of constant composition of seawater (CCSW) is valid for the major constituents. This assumption is open to question (9a); however, variations likely to be encountered are small, and the treatment that follows will result in a ratio that is itself quite insensitive to small variations in composition. With this assumption, all of the terms in parentheses in Eq. 6 are known as a function of salinity S. Both K_c and γ vary with the total ionic strength μ. Assuming CCSW, and taking as a reference seawater the synthetic seawater of Lyman and Fleming (10), the total ionic strength of a seawater is given with sufficient accuracy as a direct function of salinity,

$$\mu = k_1 S, \tag{7}$$

where $k_1 = 0.0204/‰$. The variation of K_c with μ and temperature has been measured by Cheek (11). The relation between γ and μ has been given (12), and the validity of the relation has been tested in this laboratory under the experimental conditions proposed (7). Finally, accepting 0.0668 as the probable best value (9b) for the magnesium:chlorinity ratio (Mg(g/kg)/Cl ‰) and assuming 90% of the total is not otherwise complexed (13,14), then $[Mg^{++}] = k_2 S$, where $k_2 = 1.40 \times 10^{-3}$ g-atoms per liter per unit S.

Relation Between Activity, Concentration, and Salinity–Shipboard Determination of Fluoride

At usual seawater pH, the hydroxide ion concentration is sufficiently small that it need not interfere with the electrode determination of the fluoride concentration, if the pH remains fairly constant. In stirred samples exposed to the atmosphere, however, pH decreases slowly causing drifting cell potentials. Buffering the system near pH 5 eliminates this drift. If w ml of buffer solution of known ionic strength μ_b is added to v ml of sample of ionic strength μ_w, the fluoride activity measured in such a modified sample may be related to the fluoride concentration in the original sample via the equation

$$C = a\left(\frac{w + v}{v}\right)\left(\frac{K_c[Mg^{++}] + 1}{\gamma}\right), \tag{8}$$

where K_c, γ, and $[Mg^{++}]$ all pertain to appropriate values in the sample after buffer addition, i.e., at some new ionic strength μ_{mix} and lower $[Mg^{++}]$. Replacing the known terms in Eq. 8 by $K_n(S)$, then

$$C = aK_n(S), \tag{9}$$

where S is the salinity of the original sample before buffering.

When μ_b, w, and v are fixed, $K_n(S)$ is a function of the salinity of the original sample only. Values of w, v, and μ_b are chosen to yield a minimum change in μ_{mix} with change in S and maximum fluoride concentration in buffered sample.

The relation between a and C allows standardization in terms of C. This is desirable since the closer the sample and standard are in composition, the less the liquid junction potentials will differ. Furthermore, requirements for accuracy of $K_n(S)$ are reduced. The electrode system is standardized by measuring the cell potential E_1 in a buffered synthetic seawater of known total fluoride concentration C_1 and salinity S_1 (before buffering) and computing β from

$$E_1 = \beta - \frac{RT}{F} \ln C_1. \tag{10}$$

If a seawater sample of salinity S_2 and unknown total fluoride ion concentration C_2 is similarly buffered and the cell potential E_2 measured, an approximate concentration C_x may be computed using Eq. 11 with β determined from Eq. 10,

$$E_2 = \beta - \frac{RT}{F} \ln C_x. \tag{11}$$

C_x will equal C_2 only for the special case where $S_1 = S_2$. When $S_1 \neq S_2$, C_2 is computed from

$$C_2 = Q_n C_x, \tag{12}$$

where

$$Q_n = \frac{K_n(S_2)}{K_n(S_1)}. \tag{13}$$

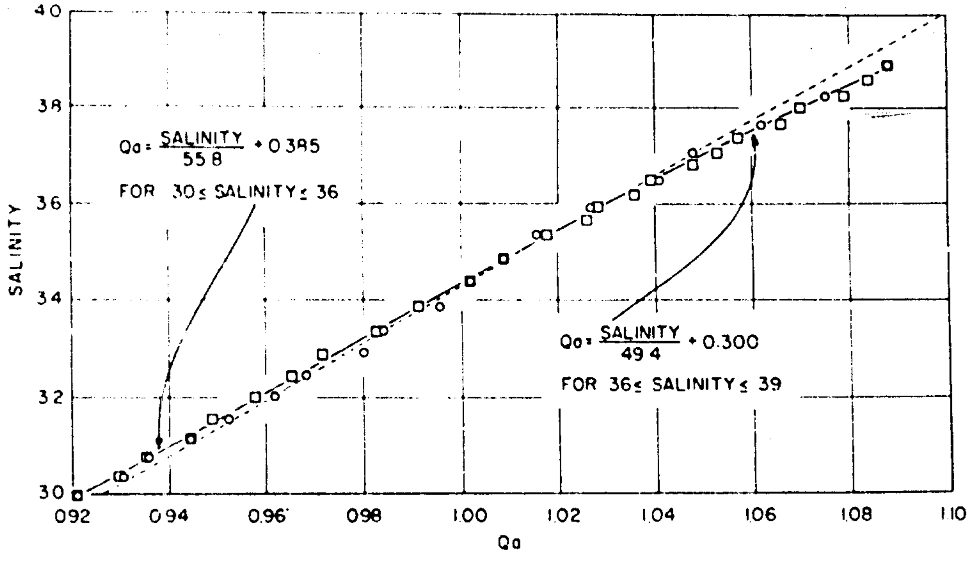

Fig. 1 - Q_n versus salinity. Experimental values for two separate runs are given by squares and circles, and the equations define the best experimental lines. The dashed line gives values calculated using Eq. 13.

When the salinities of the standardizing sample S_1 and of the unknown sample S_2 are the same, K_n is a constant, and comparing Eq. 1, 9, and 10, $\beta = \alpha + RT/F \ln K_n$ when the constant dilution factor is ignored. When $S_1 \neq S_2$, β is not constant; it is equal to $\alpha + RT/F \ln K_n(S_1)$ in the standardizing solution, but it is equal to $\alpha + RT/F \ln K_n(S_2)$ in the unknown. Rather than use the absolute values of $K_n(S)$, it is convenient to assume that β is constant and apply the correction in Eq. 12 after computing the approximate concentration C_x in Eq. 11. Computed and experimental values for $Q_n(S)$, shown in Fig. 1, are discussed in detail in a later section.

EXPERIMENTAL PROCEDURES

Reagents

Aqueous NaF standards were prepared by dilution of a 0.5M standard solution prepared by weighing Baker Analyzed Reagent Grade NaF as received. The composition of the Total Ionic Strength Adjustment Buffer (TISAB), available commercially from Orion Research, Inc., Cambridge, Mass., is given elsewhere (15); its total ionic strength was 1.9, and the buffered solutions were between pH 5 and 6.

Low-fluoride artificial seawater was prepared as described by Lyman and Fleming (10) except that all of the sulfate was added as $MgSO_4$ (which was free of any fluoride impurity). The remaining Mg was added as $MgCl_2$ (which contained 2.4×10^{-4} mole F^-/mole), and necessary NaCl was added to balance the formulation. All reagents were screened rapidly for fluoride impurities, using the method previously described (7), and all other reagents were fluoride-free except $CaCl_2$, which contained 1×10^{-4} mole F^-/mole. The finished solution contained 7 ± 3 μM/l fluoride as an impurity in other salts. A portion of this water was then spiked with NaF (to give a total fluoride content of 340 μM/l), and a series of standards was prepared by a mixture of the 340 and 7 μM standards. Determination of the fluoride content in the high-fluoride standards established that the standards were internally consistent and allowed experimental determination of the actual fluoride concentration in the low-fluoride water of 6.7 μM. The predicted salinity of the finished solution was 34.33, and the measured salinity was 34.36; its computed total ionic strength was 0.700.

Apparatus and General Procedure

The apparatus and general procedures were as previously described (7). Salinities were measured to the nearest 0.003 ‰ with an Industrial Instruments, Inc., Induction Salinometer. The Orion Model 94-09 LaF_3 electrode was used with an Orion Model 90-01 reference electrode in samples held at 25.0 ± 0.1°C, and potentials were measured with an Orion Model 801 pH meter.

Procedure for Fluoride

Pipette 25 ml of the synthetic seawater standard containing about 70 μM/l fluoride into a polyethylene beaker. Add 5 ml of TISAB, stir, and determine the cell potential E_1 after it is stable to 0.1 mv. When the sample and standard are similar in composition, values precise to 0.1 mv may be obtained in about 15 min. Calculate β in Eq. 10. Similarly pipette 25 ml of the unknown seawater sample into a beaker, add 5 ml TISAB, determine E_2, and calculate C_x in Eq. 11. Measure the salinity of the unknown, determine Q_a from the appropriate equation in Fig. 1, and compute C_2 from Eq. 12.

A thermostat is convenient but not necessary. The essential requirement is that the sample and standard be at the same temperature, between 20 and 30°C, and that the electrodes not be subjected to sudden temperature changes. With good temperature control, standards need not be checked more than once or twice a day, and E_1 and E_2 may easily be determined with a precision of 0.1 mv.

RESULTS AND DISCUSSION

If in a short period of time measurements are alternately made on a standard and an unknown and then repeated, values of E_1 and E_2 will in general be reproduced within 0.1 mv. The major sources of error are slow drifts in the reference electrode systems resulting in changes in β with time. With infrequent standardization, such drift causes deviations in the computed values of C_2 larger than short-term reproducibility would imply. Experimentally, it is convenient to standardize infrequently. Under such conditions, the probable error of an individual determination was examined by making measurements on samples of known fluoride content, so the errors, expressed as percent error, are a measure of bias or inaccuracy, not imprecision. Following Eisenhart (16), this is a case where systematic error is not negligible, and imprecision is negligible. However, over a long period of time, experiments described below showed that bias appeared to vary somewhat randomly about zero, so that probable error limits for an individual determination (when standardization is infrequent and temperature control is good) may be inferred from observed bias distribution. The assumption that data taken over a very long period of time would represent a population obeying the normal law of error is open to question. However, since the end result desired here is a reasonable estimate of probable bias, this approach was adopted as a convenient way to handle a large amount of data quantitatively, and error limits so derived should not be any less meaningful than a simple average error. The error limits appear conservative, because, as is seen below, they lie well outside the worst errors actually observed; however, the quoted deviations must not be considered true standard deviations.

Fluoride in Synthetic Seawater–Constant Salinity

Synthetic seawater standards with varying known fluoride contents were prepared as described above, and the electrode response was determined as a function of concentration and time. In each run, a single measurement, randomly located within the run and using the 73.1 μM standard, was used to determine β. The results of the measurements

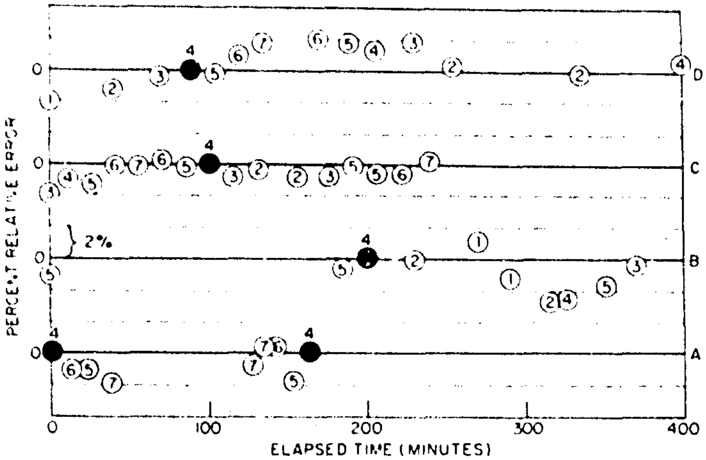

Fig. 2 - Errors caused by variation of electrode standardization with time. Concentrations of fluoride in the synthetic seawater standards used were: 1 = 6.74 μM, 2 = 37.8 μM, 3 = 56.0 μM, 4 = 73.1 μM, 5 = 113 μM, 6 = 174 μM, and 7 = 340 μM. Solid symbols show measurements used to define β for each run.

in the other standards shown in Fig. 2 were used to determine the error limits for measurements made at constant μ. In Run A, poor temperature control caused a drift in β of 0.8 mv in 160 min. Observed values in this run were corrected by assuming a linear drift of β over this period. To assess absolute inaccuracy to be expected in a typical measurement, data from these four runs were considered as one set; the standard deviation of an individual measurement from the known value was 1.2%, and the mean deviation was -0.4%, based on 45 measurements. Taking the limits of error as three times the former value, an individual measurement would be expected to be within ±3.6% of the true value in a well-thermostated system when standardization is infrequent. This is fully consistent with previous determinations of relative error limits in 1M NaCl solutions, which ranged from 5.2% to 2.3% depending on the concentration range.

These results indicate that the activity of fluoride in seawater may be measured with considerable accuracy. When the ionic composition of the sample is known, the total concentration may also be inferred. The accuracy of this inferred concentration depends on the assumption that the concept of constant composition of seawater holds approximately true. In local situations where this is not so, the calculated concentrations will be biased. It is unlikely that the relation between S and μ would be materially altered, but uncertainty in $|Mg^{++}|$ would create error. If $|Mg^{++}|$ was 5% higher than presumed in water of salinity 36 ‰, $K_n(S)$ used would be 2.2% low. An abnormally high $|Ca^{++}|$ could also cause low results due to unsuspected fluoride complexation. Hence, the error of 3.6% only applies to well-defined waters or where $|Mg^{++}|$ has been independently determined. In general use, a determination should have limits of error of ±5%, and appropriately higher limits must be used in unusual areas. Certain preliminary results suggest that wider error limits may apply to deep-water samples.

A Priori Calculation of Q_n

Values of $K_n(S)$ were computed using the realtion defined in Eqs. 8 and 9 for the specific case where S_1 = 34.325 ‰, μ_1 = 1.9, and v = 5w. The true relation between μ and γ becomes increasingly uncertain as μ increases, due to difficulties in the absolute determination of liquid junction potential differences encountered in measurements at different values of μ, particularly in complex ionic media such as seawater. If the standard and unknown are of very similar ionic makeup, however, this uncertainty can be largely eliminated by accepting an experimentally determined value of γ at a single ionic strength that includes a small, unknown, but constant, contribution from liquid junction potentials. Then γ at other values of μ may be determined from the available $d\gamma/d\mu$ data and the single fixed reference point. This procedure has been followed here.

The electrode system was standardized in pure NaF standards as previously described, and α was determined in Eq. 1. The system was then standardized in the buffered seawater standard, and β was determined in Eq. 10. Repeated determinations yielded $\beta - \alpha = 34.5$ mv, uncertain by about ±0.2 mv, which corresponds to an experimentally determined $K_a(S = 34.325)$ of 3.83 and hence of an effective γ of 0.538 when $\mu_{mix} = 0.900$; γ at other values of μ_{mix} was obtained from the existing $d\gamma/d\mu$ data. Resulting $K_a(S)$ and corresponding $Q_a(S)$ values are given in Table 1. Note that the value selected for γ does not materially affect the accuracy of determinations of fluoride concentration in seawater when the standard is synthetic seawater. In this case, the absolute values appear in a quotient, and only the ratio between them, related to $d\gamma/d\mu$, is significant. The value of γ becomes significant only when the relation between activity and concentration is required. Hence, these values of Q_a will also apply when other reference electrodes are used. When experimentally determined values of Q_a are available as determined in the next section and shown in Fig. 1, greater accuracy is obtained by using these in preference to calculated values; however, the differences are not large.

Table 1
Calculated Values of Q_a as Function of Salinity*

Salinity	$[Mg^{++}]$	μ_{mix}†	γ	K_c	K_a	Q_a
30.0	0.035	0.83	0.55	18.2	3.56	0.93
32.0	0.038	0.86	0.55	18.0	3.67	0.96
34.0	0.040	0.89	0.54	17.8	3.80	0.99
34.325	0.040	0.90	0.54	17.8	3.83	1.00
36.0	0.042	0.93	0.53	17.7	3.94	1.03
38.0	0.045	0.96	0.53	17.5	4.07	1.06
40.0	0.047	1.00	0.52	17.4	4.22	1.10

*$S_1 = 34.325$, $\mu_b = 1.9$, and $w = 5v$.
†Definitions of symbols are given in text.

The function $Q_a(S)$ changes slowly with salinity, and because it is a quotient, it is important that slopes be known, but it is insensitive to errors in the absolute magnitudes of the quantities determining $K_a(S)$. This is an important advantage in view of the many assumptions involved and the rather large uncertainties in some of these quantities.

Fluoride in Mediterranean Seawater—Variable Salinity

The sample used was taken May 18, 1967, at 32°51'N, 30°47'E, 500 M depth, and stored in Pyrex until used. After standardization, E_2 was measured, and C_x was determined in the buffered sample and in this same sample after successive dilutions with a 5:1 mixture of water and buffer. Salinities in the diluted samples were calculated on the basis of the known dilution ratios, and the fluoride content of the sample was computed from E_2 obtained at $S_2 = S_1$, where $C_x = C_2$, and the true C_2 was computed at other dilutions. From known C_2 and measured C_x, experimental values of Q_a were computed using Eq. 12. These experimentally determined values of Q_n for $29.9 < S_2 < 38.9$ are shown in Fig. 1 connected by solid lines. The results of two entirely independent determinations are shown, and the equations give the best experimental values of Q_a. The theoretical values of Q_n, calculated as in Table 1 for every 1 ‰ of salinity, are reproduced within 0.004 by $Q_n(S) = \text{salinity}/57.9 + 0.408$. The dashed line in Fig. 1 gives these predicted values.

The calculated and experimental values of Q_n agree very closely. They differ by no more than 0.002 for $32 < S_2 < 37$; the maximum deviation in the calculated value of Q_n is -0.008 at $S_2 = 38.9$ and +0.004 at $S_2 = 30$. This indicates that Eq. 8 includes the important variables, the observed deviations probably being due to uncertainities in the various terms. Similar values of Q_n can be computed for other values of S_1, v, w, and μ_b, if necessary. The experimental values may be used with confidence over the tested range, and a short extrapolation to $S_2 = 40$ is probably valid.

If we assume that the fluoride determination in the Mediterranean water at S = 34.325 ‰ is accurate, i.e., where $S_2 = S_1$, and that experimental values of Q_n are known, the error contributed by measuring at a salinity different from that used to standardize may be assessed. Over the salinity range examined, fluoride ranged from 61.5 to 79.9 μM/l. For 25 determinations, the mean error was -0.07%, and the standard deviation of the bias was 0.17%. This is small compared to the 1.2% standard error of the bias obtained in Fig. 2 and shows that when experimental values of Q_n are used, no significant additional uncertainty is added when standardizing at one salinity and measuring in real waters at other salinities.

Recovery of Added Fluoride, Atlantic Seawater

Fluoride was determined in a seawater sample (26° 35'N, 74°48'W, 4600 m, S = 36.115°/oo). A known amount of fluoride was added to a portion of the water, taking care to keep other parameters constant, and a series of solutions was prepared containing known increments of fluoride. Total fluoride was measured, and the recovery was calculated. Results are given in Table 2.

Table 2
Recovery of Fluoride Added to Seawater

Fluoride Added to Sample (μM/l)	Measured Concentration (μM/l)	Fluoride Recovered (μM/l)	Error (%)
0	74.5	-	-
30.0	104.7	30.2	+0.7
58.6	132.9	58.4	-0.3
85.3	159.1	84.6	-0.8
110.7	183.6	109.1	-1.6

Absolute Accuracy Check

Fluoride was determined in Atlantic seawater (26°N, 80°W, 30 m deep), which had previously been analyzed by Wilkniss and Linnenbom (4) using photon activation analysis. They found 1.35 ± 0.18 μg/ml. Using the LaF_3 electrode, fluoride found was 1.41 ± 0.07 μg/ml. Both errors are limits of error taken as three times the standard deviation from the mean in the former case and ±5% in the latter case. Between analyses, the sample was stored in a tightly stoppered polyethylene bottle that was opened only a few times. A comparison of salinities taken at the time of sampling and measurement verified that little change in the sample composition had occurred, and appropriate corrections were made for the small water loss involved of 0.2%.

The fluoride electrode yields results of slightly lower accuracy than the spectrophotometric method of Greenhalgh and Riley (3). They evaluated accuracy by determining recoveries of added fluoride from a seawater. To allow comparison of their results with those presented here, their recovery data were converted to percent error and a "standard deviation of the bias" computed, where all of the qualifications previously stated apply. For nine determinations the standard deviation of the relative bias was 1.3%, and the mean error was -0.2%. This compares with a bias standard error here of 1.2% and a mean error of -0.4%. When the method was later applied to the Autoanalyzer (17), the relative standard deviation was ca. 0.9%, and the average of a number of replicate analyses of an artificial seawater containing known amounts of fluoride was not detectably biased. The method of Wilkniss and Linnenbom is less precise but has the advantage of being an absolute method for total fluoride.

For highest accuracy the system must be thermostated. Measurements made at ambient temperatures in a room where the rate of temperature change does not exceed 1°/hour may be made almost as accurately with frequent standardization. Sudden thermal shocks must be avoided; attendant changes in β persist for several hours. For measurements where both sample and standard are seawaters, other reference electrodes, such as the saturated calomel electrode, give comparable results.

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13. ABSTRACT

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