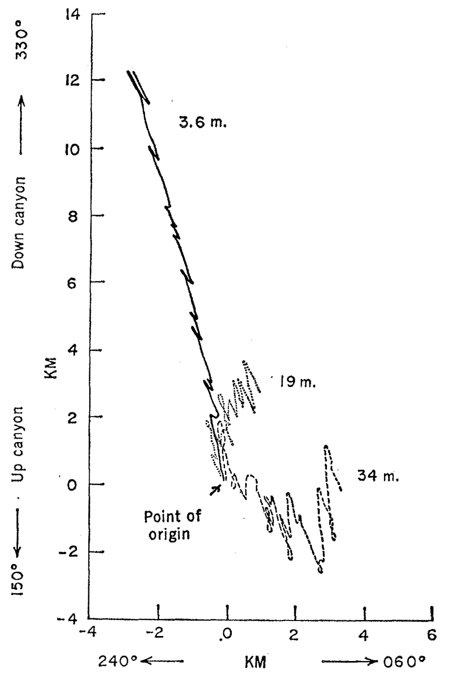

Fig. 2. Trajectories of the movement of particles of water at three depths above the floor of La Jolla Canyon where the axis is 206 m deep.

to downcanyon are generally slow, but are much more rapid than are changes from downcanyon to upcanyon.

Virtually all higher speed currents occur during ebb tides in the Scripps and La Jolla canyon records (Fig. 1B). Many of the peaks clearly have a tidal cycle, although others are associated with changes of direction of short duration that are not related to the tide. The currents on the ridge have peaks in a southerly direction during most of the ebb tides, indicating that these do have a tidal relation.

Plots of the total movement or trajectory of currents near the floor of a canyon show a large residual in the downcanyon direction. Superimposed records of three current meters (Fig. 2) indicate a large net movement downcanyon near the floor. Slight net movement downcanyon occurred 19 m above the bottom, and at 34 m the movement was at first toward shore and then it reversed, so that a water particle would have had no net axial transport. As distance above the canyon bottom increases, net transport becomes more related to ordinary tide-influenced oceanic patterns (*4*).

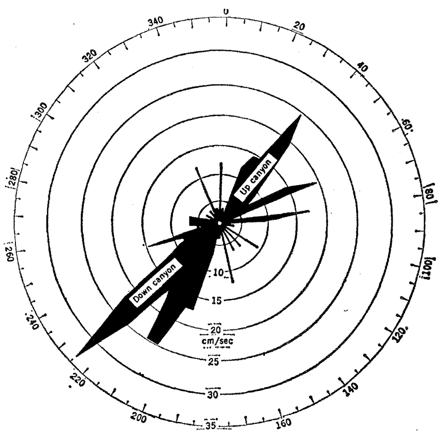

Fig. 3. Vectoral components of current at a depth of 107 m near the floor of Scripps Canyon from 13 to 18 December 1968.

Currents may also be examined by constructing a vector rose of velocities. One such record includes the highest velocity we have observed to date, which was downcanyon (Fig. 3). Some unusual directions are related to periods of changing direction, and others may be small transverse oscillations conceivably related to the passing of large fish, but the greater part of the currents are up- and downcanyon. This would be expected because of the narrowness of the canyon.

During 34 percent of the time we recorded, flow was downcanyon; 42 percent of the time, flow was upcanyon; and during the remaining 24 percent of the time it was changing direction. Currents capable of eroding sand (over 18 cm/sec) make up 4.8 percent of all recorded flow time, or 14.4 percent of downcanyon flow time. Erosive currents upcanyon occur, but they are negligible in number and duration. Net transport is always downcanyon since average downcanyon flow is 8.25 cm/sec, whereas average upcanyon flow is 1.85 cm/sec. Downcanyon flows last 47 minutes on the average, and upcanyon flows last for an average of 74 minutes.

Although many changes in direction appear to show no periodicity, we have found several cases in which reversals occurred at periods of about 4 hours. A similar period has been found in studies of internal waves at the U.S. Navy platform off Mission Beach, California (*5*).

We have compared current velocities during periods of spring tides to those during neap tides and have failed to find any relationship. Similarly, we could find little difference between currents related to periods of rapidly falling or rapidly rising tide as compared to periods of slow tidal changes or to extreme spring tides (Fig. 1).

As yet we have not had the opportunity to obtain a record during unusually large waves. There are some indications that considerably higher velocities may exist during storms, and we hope to test this. However, we have clear evidence that the normal current velocities are capable of moving considerable quantities of sand down the axis of a canyon (*6*). These currents are entirely different from powerful turbidity currents.

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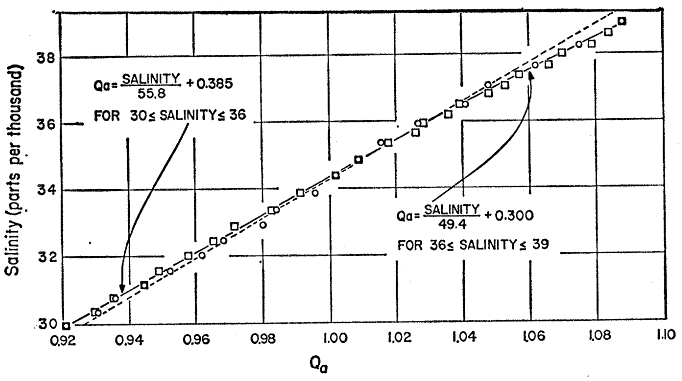
17 March 1969; revised 1 May 1969

Fluoride in Seawater: Measurement with Lanthanum Fluoride Electrode

Abstract. *Fluoride ion concentrations are quickly and easily determined in seawater by means of a fluoride-selective electrode. Samples require little pretreatment; a determination takes 15 minutes; error limits are 5 percent; equipment required is rugged, inexpensive, and motion-insensitive; and minimum demands are made on the operator.*

Specific-ion electrodes offer an attractive approach to the analysis of minor constituents in complex solutions. The determination of fluoride in seawater is a representative problem of particular interest because fluoride may not be a conservative constituent (*1*). Using an Orion model 94-09 LaF_3 electrode with an Orion model 90-01 reference electrode, I have measured fluoride concentrations directly in synthetic and natural seawaters. The method permits simple compensation for variation in salinity and is designed for easy adaptation to measurements *in situ*.



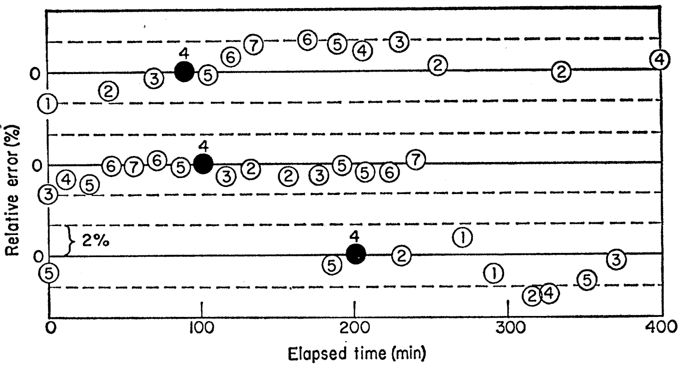


Fig. 1 (left). Values of Q_a plotted against salinity. Experimental values for two separate runs are given by squares and circles, and the equations define the best experimental lines. The dashed line gives values calculated from Eq. 10. Fig. 2 (right). Error caused by variation of electrode standardization with time. Concentrations of fluoride in the synthetic seawater standards used (in micromoles per liter) were: 1 = 6.74; 2 = 37.8; 3 = 56.0; 4 = 73.1; 5 = 113; 6 = 174; and 7 = 340. Filled circles show measurements used to define β for each run.

Fluoride may be determined by first adding v milliliters of synthetic seawater of salinity S_1 and total fluoride ion concentration C_1 (all concentrations are in moles per liter) to w milliliters of a buffer solution of known total ionic strength μ_b that will buffer the system between pH 5 and 6. A suitable buffer is TISAB (total ionic strength activity buffer) with $\mu_b = 1.9$ (*2*). The electrode system may be standardized in this sample by determining cell potential E_1, and the constant β may be computed from the relation

$$E_1 = \beta - (RT/\mathbf{F}) \ln C_1 \qquad (1)$$

where R, T, and **F** are the gas constant, absolute temperature, and the faraday, respectively.

In a similar manner, to v milliliters of a seawater sample of salinity S_2 and unknown total fluoride ion concentration C_2, w milliliters of the same buffer may be added; using the value of β determined from Eq. 1, one may measure E_2 and calculate C_x from the equation

$$E_2 = \beta - (RT/\mathbf{F}) \ln C_x \qquad (2)$$

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

$$C_2 = Q_a C_x \qquad (3)$$

where Q_a, whose identity is discussed in more detail below, is a function of S_2 and S_1.

Variation of Q_a with salinity was measured at 25.0°C for a sample of eastern Mediterranean seawater (32°51′ N, 30°47′E, depth 500 m) with an initial salinity of 38.94 parts per thousand. Keeping $v/w = 5$, successive measured volumes of distilled H_2O plus buffer were added and E was measured at various salinities down to 29.9 parts per thousand. The actual fluoride concentration of 70.6 μmole/liter was computed at $S_2 = S_1$ where $C_x = C_2$, and C_2 was calculated at the other dilutions. From the measured values of C_x and known values of C_2, the experimental values of $Q_a(S)$ shown in Fig. 1 were determined. The standardizing solution was Lyman and Fleming synthetic seawater (*3*) which had a known fluoride concentration of 73.1 μmole/liter and a salinity of 34.33 parts per thousand.

When ionic compositions of sample and standard differ, then the term Q_a becomes necessary because the ratio of fluoride activity a to total fluoride concentration differs in the two solutions. Electrode response is accurately given (*4, 5*) by the Nernst relation

$$E = \alpha - (RT/\mathbf{F}) \ln a \qquad (4)$$

where α depends on the reference electrodes and on liquid junction potentials in the cell. The ratio of activity to concentration is obtained as a function of salinity by assuming the constant composition of seawater (CCSW). This assumption is open to question (*6*); however, variations likely to be encountered are small. Fluoride activity depends on the concentration of free uncomplexed fluoride in solution $[F^-]$ and its activity coefficient γ

$$[F^-] = a/\gamma \qquad (5)$$

The relation between γ and total ionic strength μ (*7*) has been tested (*5*), and the total ionic strength of seawater is given with sufficient accuracy as a direct function of salinity S, that is, $\mu = 0.0204\ S$ (in parts per thousand), if we assume CCSW. Hence the relation between a and $[F^-]$ is known in waters of different salinity.

Part of the total fluoride concentration is bound in the MgF^+ complex according to the equilibrium

$$Mg^{2+} + F^- \rightleftharpoons MgF^+ \qquad (6)$$

with a concentration formation constant

$$K_c = \frac{[MgF^+]}{[Mg^{2+}][F^-]} \qquad (7)$$

where $[Mg^{2+}]$ is the concentration of Mg^{2+} not bound up in other complexes and is taken (*8*) as 90 percent of the total Mg concentration in seawater. If we again assume CCSW and accept 0.0668 (*6*) as the probable best value

Table 1. Calculated values of Q_a as a function of salinity. Salinity S_1 = 34.325 parts per thousand; total ionic strength μ_b = 1.9; and $w = 5v$.

Salinity (parts per thousand)	$[Mg^{2+}]$ (Mole/liter)	Ionic strength μ_{mix}	Activity coefficient γ	K_c	K_a	Q_a
30.0	0.035	0.83	0.55	18.2	3.56	0.93
32.0	.038	.86	.55	18.0	3.67	.96
34.0	.040	.89	.54	17.8	3.80	.99
34.325	.040	.90	.54	17.8	3.83	1.00
36.0	.042	.93	.53	17.7	3.94	1.03
38.0	.045	.96	.53	17.5	4.07	1.06
40.0	.047	1.00	.52	17.4	4.22	1.10

for the ratio of Mg (in grams per kilogram of seawater) to Cl (in parts per thousand), then [Mg^{2+}] is also known as a function of salinity. Finally, K_c depends on μ and hence on S; its dependence has been determined by Cheek (*9*).

If we combine Eqs. 5 and 7 and note that $C_{F^-} = [F^-] + [MgF^+] = [F^-](1 + K_c[Mg^{2+}])$, the relation between the fluoride activity sensed by the electrode in the buffered solution and the total inorganic fluoride in the sample before dilution C_{F^-} is given by a function $K_a(S)$ which depends only on salinity

$$C_{F^-} = a_{F^-}\left(\frac{w+v}{v}\right)\frac{(1 + K_c\,[Mg^{2+}])}{\gamma_{F^-}} \quad (8)$$

Thus

$$C_{F^-} = a_{F^-}\,K_a\,(S) \quad (9)$$

where K_c, γ_{F^-}, and [Mg^{2+}] all pertain to the sample after addition of buffer, that is, at some new ionic strength μ_{mix} and lower [Mg^{2+}].

When salinities of the standard and of the unknown are the same, K_a is a constant, and, based on a comparison of Eqs. 1, 4, and 9

$$\beta = \alpha + (RT/\mathbf{F})\ln K_a$$

When $S_1 \neq S_2$, β is not constant and is given by

$$\beta = \alpha + (RT/\mathbf{F})\ln K_a(S_1)$$

in the standardizing solution, but in the unknown by

$$\beta = \alpha + (RT/\mathbf{F})\ln K_a(S_2)$$

Rather than use the absolute values of $K_a(S)$, it is convenient to assume a constant value of β and to apply the correction after computing the approximate concentration C_x, as in Eq. 2, and then to apply the correction in Eq. 3, where

$$Q_a(S) = K_a(S_2)/K_a(S_1) \quad (10)$$

The function $Q_a(S)$ changes slowly with salinity, and, because this function is a quotient, it is important that slopes be known; however, $Q_a(S)$ is insensitive to errors in the absolute magnitudes of the quantities that determine $K_a(S)$.

Values of $Q_a(S)$, calculated from Eqs. 8 through 10, are given in Table 1. An effective γ (including contributions from the liquid junction potential) was experimentally measured at $\mu_{mix} = 0.900$; γ at other values of μ_{mix} was calculated from existing $d\gamma/d\mu$ data. The calculated and experimental values of Q_a (Fig. 1) are in good agreement. They differ by no more than 0.002 for $32 < S_2 < 37$ parts per thousand; the maximum deviation in $Q_{a,calc}$ is -0.008 at $S_2 = 38.9$ parts per thousand and $+0.004$ at $S_2 = 30$ parts per thousand. The calculated values are reproduced to within 0.004 by

$$Q_a(S) = (\text{salinity}/57.9) + 0.408$$

Similar values of Q_a can be computed for other values of S_1, v, w, and μ_1, if necessary.

Error in fluoride determinations is primarily due to the drift of standardization with time. Stability and reproducibility of electrode response is shown in Fig. 2 for samples of synthetic seawater of constant salinity (*3*) maintained at 25.0°C. In each run the electrodes were standardized just once, and concentrations in other samples were computed on the assumption of a Nernstian response. The difference between measured and known C_{F^-} was expressed as the percentage of relative error. The relative standard deviation of an individual measurement from the true value was 1.2 percent, based on 45 measurements, and mean deviation was -0.4 percent. Real seawater (salinity = 36.12 parts per thousand, C_{F^-} = 74.3 μmole/liter) spiked with additional fluoride yielded a relative standard deviation of the measured fluoride from true fluoride of 0.6 percent based on five measurements between 74 and 183 μmole/liter. Analysis of the data (Fig. 1) indicates that uncertainties involved in the use of Eq. 3 do not materially degrade precision when experimental values of Q_a are used. For 25 determinations the relative standard deviation of an individual measurement was 0.2 percent. Accuracy of concentrations inferred in natural waters depends on the validity of the CCSW assumption. If we combine the above errors with the probable maximum variation in the ratio of Mg to Cl, the limits of relative error for measurements in real waters having variable salinity may be taken as about 5 percent. For atypical waters the technique cannot be used without additional data.

The validity of Eqs. 1 through 3 was verified by determining C_{F^-} in a single sample of Atlantic seawater (salinity 36.15 parts per thousand) by two independent methods. Photon activation analysis (*10*) indicated a fluoride concentration of 1.35 ± 0.18 μg/ml; with the LaF_3 electrode, the concentration found was 1.41 ± 0.07 μg/ml, both errors being limits of error.

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25 November 1968; revised 10 April 1969 ■

Water Vapor: Observations of Galactic Sources

Abstract. *We measured the emission of water vapor at a wavelength of 1.35 centimeters from nine sources with the 120-foot (36.5-meter) Haystack antenna. Eight sources lie within 30 seconds of arc of the hydroxyl sources of 18 centimeters but not all hydroxyl sources produced detectable emission of water vapor. All sources are smaller than 30 seconds of arc in angular diameter, but we resolved at least three separate sources in the Orion Nebula. We do not find that the known hyperfine components are present with the equilibrium intensity distribution.*

Microwave emission by interstellar water vapor by virtue of the rotational transition at a wavelength of 1.35 cm has been discovered by Cheung *et al.* (*1*) and further studied by Knowles *et al.* (*2*). We now report independent observations of the emission by interstellar H_2O which confirm and extend the previous results. Our observations show that (i) the emission from the Orion