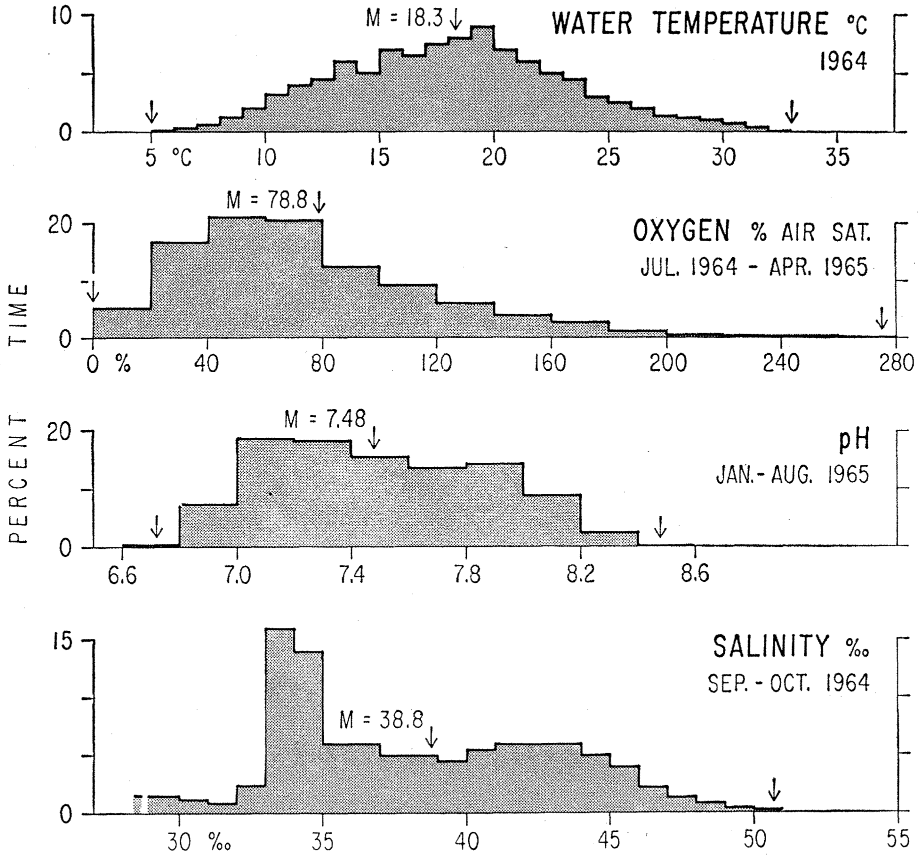

Fig. 3. Time durations, extremes, and means of values of water temperature, oxygen, *p*H, and salinity in marine marsh, Mission Bay, California.

100 percent saturation about 75 percent of the time during a 9-month period. The significance of this is not known, because there is little experimental evidence on oxygen consumption by foraminiferans under different conditions.

The *p*H values ranged from 6.7 to 8.5, with most values greater than 7.0 but markedly less than the *p*H of sea water in the adjacent bay. These *p*H values, which are lower than sea water, represent a marsh chemistry which probably is an important restricting factor on organisms. Laboratory experiments have been designed to test the physological effect of *p*H.

Salinity, with accurate continuous recordings for only 2 months, ranged from less than 30 parts per mil to more than 50 parts per mil. Salinities were higher than those of the bay about 75 percent of the time and were higher than 40 parts per mil about 37 percent of the time.

These preliminary results do not apply to every marine marsh, but similar values may be expected in many other marshes. The most striking result is the great range in values of some of the important environmental parameters measured, and this is probably a general characteristic of marshes. It is believed that the general approach we have used is a reasonable method for defining sedimentary and biological marine environments.

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20 September 1966

Electrode for Sensing Fluoride Ion Activity in Solution

Abstract. *Electrodes constructed from single-crystal sections of rare earth fluorides respond to fluoride ion activity over more than five orders of magnitude and show a high selectivity for fluoride over other common anions. These electrodes can be used for either direct measurement of fluoride ion activity or detection of the end point in titration.*

There has been no way of determining fluoride single-ion activities in aqueous solution, although such measurements are of obvious interest in studying fluoride complexes in solution, in following uptake and metabolism in both plants and animals, and in similar applications. Furthermore, the analysis of drinking water and body fluids for low concentrations of fluoride has been a tedious procedure, usually requiring a distillation step to eliminate interferences (*1*).

We report the development of an electrode-type of sensor, which will give a Nernstian response over a wide range of fluoride ion activity and which is highly selective for fluoride in the presence of many ions commonly found in public water supplies and biological systems.

Construction of the electrode is similar in principle to that of a conventional glass *p*H electrode, except that the membrane material is a disk-shaped section of single-crystal rare earth fluoride, such as LaF_3, NdF_3, or PrF_3. The section, typically 1 cm in diameter and 1 to 2 mm in thickness, is sealed to the end of a rigid polyvinyl chloride tube with epoxy cement. The only critical step is assembling the electrode so that the seal is watertight. The tube is filled with a solution containing both fluoride and chloride ions (typically $0.1M$ NaF and $0.1M$ KCl), and electrical contact is made with a silver–silver chloride wire. The electrode is calibrated on known sodium or potassium fluoride solutions and used with an external reference electrode, such as the saturated KCl-calomel type that we used. Electrode potentials were attained rapidly and were stable. Measurements were reproducible to within less than 1 mv.

Pure rare earth fluorides are unique among known crystalline materials in having a high electrical conductance that results from mobile fluoride ions

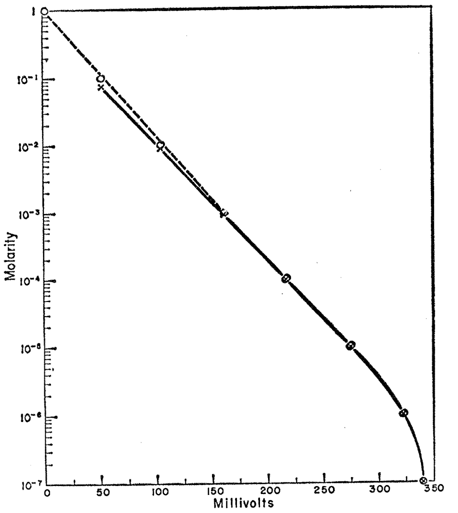

Fig. 1. Electrode response to fluoride concentration (dashed line) and calculated activity (solid line) in pure KF solutions. No estimate of single-ion activity at 1*M* was available from other data, hence only the concentration value is shown.

in the crystalline lattice (*2*). We found that a further increase in conductivity can be obtained by doping with a divalent ion such as Eu++.

Since the crystal membrane is permeable only to fluoride ions, the cell potential (*E*) is given by the Nernst equation:

$$E = \alpha - RT/\mathrm{F} \ln (\mathrm{F}^- \text{ activity in sample})$$

The value of α depends on the choice of internal and external reference electrodes and the fluoride activity in the internal electrode solution. Except for a small liquid-liquid junction potential contribution, α is constant and independent of composition of the sample. The electrode will be ideally selective for fluoride ions over those ranges of sample composition in which the rare earth fluoride is stable and has a negligible solubility. The low solubility product of crystalline LaF_3 (approximately 10^{-29}), for example, permits the use of electrodes based on it over a wide *p*H range and in the presence of many ligands that form stable complexes with La+++.

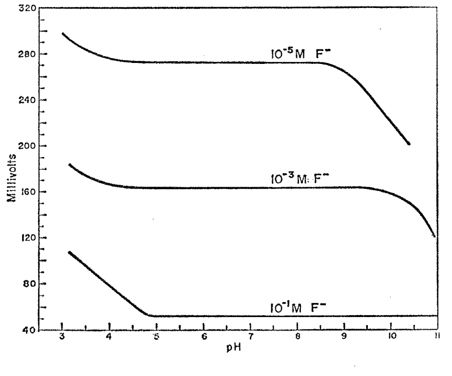

Fig. 2. Electrode response as a function of *p*H and fluoride concentration. Hydroxyl ion interference depends on the fluoride level. Decreased F$^-$ activity in acid solutions is attributed to formation of associated species.

Response of the LaF_3 electrode to concentration of F$^-$ ions is shown in Fig. 1. From a concentration of 1 to below $10^{-5}M$, the response is Nernstian and, to the extent that fluoride ion activities can be estimated from other data (*3*), appears to be close to theoretical. The concentration of F$^-$ in drinking water is about $5 \times 10^{-4}M$, and since the electrode has a usable response to approximately $10^{-6}M$, it should be of value for determinations of fluoride activity in water supplies as well as for many other determinations.

Other common anions can be virtually neglected. For example, adding 0.1*M* NaCl or $NaNO_3$ to a solution containing $10^{-4}M$ fluoride ion results in a 7-mv decrease in fluoride activity. This suppression is to be expected from the increase in ionic strength and suggests that the electrode is insensitive to a thousand-fold excess of these ions. At 10,000 : 1 (that is, $10^{-4}M$ F$^-$ in 1*M* Cl$^-$ or NO_3^-) the activity is depressed approximately 20 mv, which agrees within about 10 percent with our estimate of the activity coefficient at this level (based on fluoride activity measurements in pure solution). In the case of $SO_4^=$, $10^{-4}M$ shows only activity suppression in $10^{-1}M$ $SO_4^=$; at 1*M* $SO_4^=$, the activity suppression is 13 mv rather than the estimated 18 mv for monovalent electrolytes, but it is difficult to determine whether this represents an electrode response to sulfate or whether the electrode is still sensing the correct activity.

The only significant interference comes from hydroxide ion, which is not surprising in view of the similarities in charge and ionic radii (*4*). In pure solutions, significant hydroxide interference occurs when the concentration of hydroxide about equals the concentration of fluoride, and a tenfold excess of hydroxide will double the apparent fluoride content. In most applications this selectivity should be adequate, and, if not, independent measurements or adjustment of OH$^-$ can easily be made.

Figure 2 shows the behavior of the electrode as a function of *p*H and concentration of fluoride. As would be expected from the selectivity described above, hydroxide interference becomes more serious in dilute solutions of fluoride. At the concentrations of fluoride in drinking water, there is no interference until a *p*H of about 8.5 is reached; most public water supplies are probably in this category (*5*). The decrease in activity that occurs in the region of *p*H 4 to 5 is not artifact, but reflects the fact that the *p*K of HF is 3.14 (*4*). Other F$^-$ complexes, such as H_2F_2, may also contribute to the decrease in F$^-$ activity, particularly in more concentrated solutions.

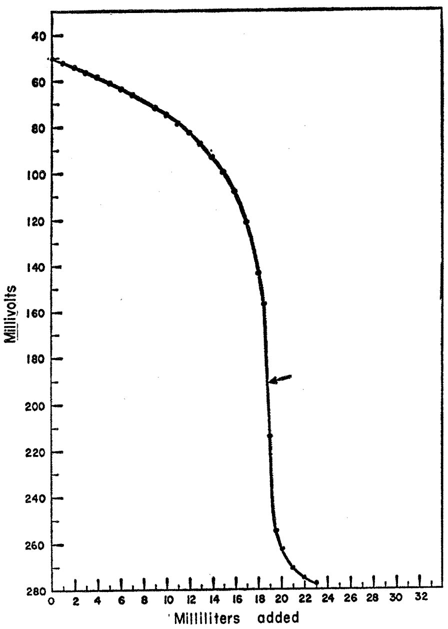

Fig. 3. Titration of NaF with $La(NO_3)_2$; the new electrode was used as an end-point detector. The arrow indicates the calculated end point. For details, see text.

Where a knowledge of concentration rather than activity is desired, or greater precision is needed, the electrode can be used as the end-point indicator with ligands that form fluoride complexes or precipitates. As an example of this, a solution that was 0.114*M* in F$^-$ and 0.1*M* in Cl$^-$, *p*H 9, was titrated with 0.101*M* $La(NO_3)_2$, *p*H 4; the results are shown in Fig. 3. The electrode gives a sharp end point that agrees with the calculated end point. Presumably other titrants such as Th(IV) or Zr(IV) would perform similarly, but this has not been studied.

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21 June 1966

Sonic Detection of a Fresh Water–Salt Water Interface

A sound wave transmitted from one medium to another of different physical characteristics will be partially reflected, depending on the properties of the two media and upon the thickness of the mixing volume between them. The strength of the reflection at a plane boundary layer depends on the difference in density, the difference in sound velocity, and the thickness of the mixing layer. Usually the temperature and salinity gradients in the open ocean are not sufficiently abrupt to produce an echo of detectable amplitude with conventional sonar of long pulse duration.

The depth of the Charles River basin is controlled by a lock which connects the basin to Boston Harbor. When the tide is high, the lock introduces a considerable quantity of salt water with each operation. The cold salt water apparently flows under the fresh water and, under drought conditions, may attain a considerable depth.

It has been found that the layer between salt and fresh water can be seen in some areas of the Charles River basin by a 12-kc sonar (*1*) of 0.1-msec pulse duration and recorded on an Alden chart. For example, the sonar records (Fig. 1) show a faint salt-fresh water interface at the start in the main basin. At this time, the depth of the interface from the surface is about 3.3 m in the main basin of the river. The boat entered the sailing lagoon at the east end of the basin (*A*) where the underwater dykes between the islands form a closed lagoon. The salt layer is 2.4 m down inside this lagoon and extends to the end of the lagoon at the dyke on the north side.

Notice should be taken of the irregular shape and the variable intensity of the interface sonar record. Perhaps there are intermittent clumps of material, with echo-producing properties, floating at the interface. Perhaps there is intermittent mixing of the fresh and salt water, with a thick gradual gradient between.

The short-pulse sonar system appears to be a useful method of finding fresh-salt water interfaces in rivers and in offshore aquifers. For example, a sonar presenfation of the sewer outlet near Deer Island light in Boston Harbor shows where warm fresh water pours into cold salt water. A column of fresh water can be seen rising to the surface and drifting away with the tide.

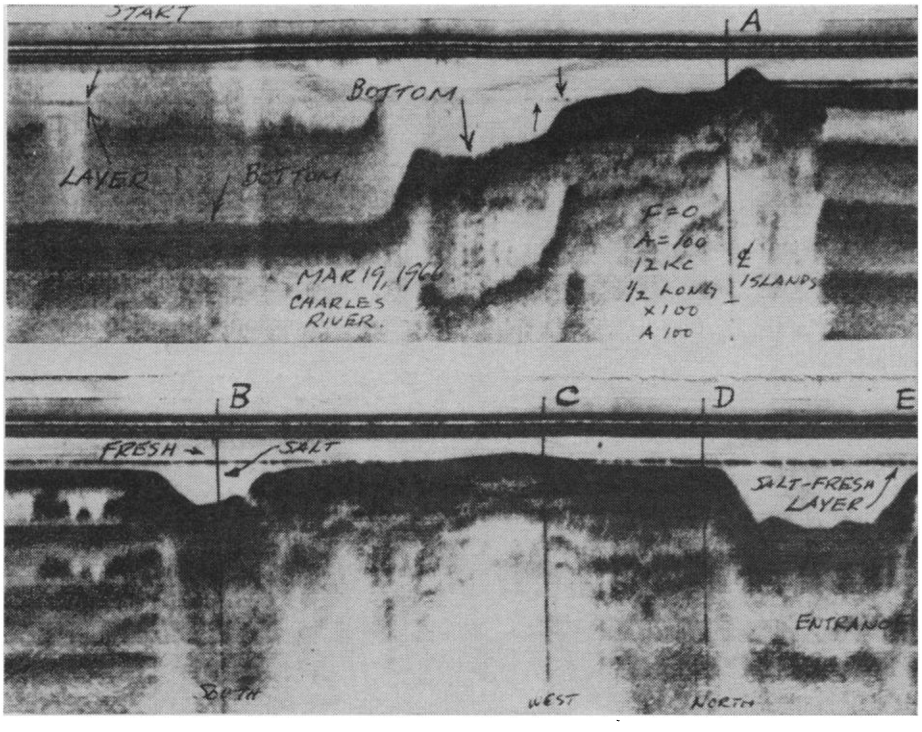

Fig. 1. Sonar records.

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3 August 1966

Ice Nuclei from Automobile Exhaust and Iodine Vapor

Abstract. *When exposed to a trace of iodine vapor, the submicroscopic particles of lead exhausted by automobiles produce nuclei for the formation of ice crystals. Concentrations of particles exceeding* 10^6 *per liter can be directly sampled from the exhaust pipe of an idling motor. Concentrations of from* 10^4 *to* 10^5 *per liter have been found in rural air downwind of auto roads; the concentration at one rural site has increased by an order of magnitude in 13 years. The phenomenon may provide a method of modifying clouds, and of determining (and monitoring) the percentage of automobile exhaust in a polluted atmosphere. It may be an important factor in inadvertent modification by man of the climate.*

A newly discovered phenomenon produces concentrations of ice-crystal nuclei (see cover) as high as 10^6/liter in the free atmosphere where automobiles have been operating. The phenomenon may provide an important new technique for extensive overseeding in supercooled clouds; it may also present a highly sensitive and simple method for detecting submicroscopic particles of lead in auto exhaust, and thus provide a practical technique for establishing an auto-exhaust index in polluted air. It may also elucidate in an unexpected way the manner in which man is inadvertently modifying atmospheric clouds over extensive areas of the United States.

In the simplest terms, the phenomenon depends on the formation of less