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THE SPECTROPHOTOMETRIC DETERMINATION OF FLUORIDE IN SEA WATER:

BY

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ABSTRACT

The zirconium-alizarin sulfonate indicator of Lamar has been applied to the spectrophotometric determination of fluoride in sea water and has been shown to be suitable. Calibration curves have been prepared for different chlorinities. The variation of apparent fluoride content with chlorinity is less than that reported by Thompson and Taylor with their reagent. Borate, iron and phosphate have been shown not to interfere at the concentrations found in sea water, while a method has been given to take care of varying alkalinites. The effects of time, temperature and light upon the color intensity have been discussed. Increased accuracy is attained through the measurement of the color intensity spectrophotometrically.

INTRODUCTION

The fluoride content of sea water has been determined colorimetrically by a method developed by Thompson and Taylor (6) in which the reagent is a reddish zirconium-alizarin sulfonate lake formed by the reaction of zirconium nitrate and alizarin sulfonate. Fluoride, in the presence of acid, reacts with and destroys this reddish lake, forming colorless zirconium fluoride and yellow alizarin sulfonate. The fluoride content is determined by measuring this bleaching of the lake.

Since the work of Thompson and Taylor (6) in 1933, no work on the zirconium-alizarin sulfonate method of determining the fluoride content in sea water has been reported in the literature, though many modifications of the method have been reported for fresh waters, starting with that of Sanchis (4). Lamar (2), in his work on fresh waters, used a reagent containing sulfuric acid to lessen the interference of sulfate in the water; this is one of the most active interfering substances in the fluoride determination. In ocean waters there is considerable sulfate and in coastal waters its concentration varies widely, thus making difficult the compensation for its interference. It was thought that use of Lamar’s indicator might well reduce the effect of sulfate in marine waters. The study of the use of this indi-

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cator was done spectrophotometrically to get greater accuracy and to eliminate the necessity for the preparation of reference standards, as is the case when using Nessler tubes. The results of this investigation are reported in this paper.

**SOLUTIONS AND CHEMICALS**

All chemicals used in this investigation were C. P. Grade.

**Indicator:**

(A) 1.840 g of ZrO(NO$_3$)$_2$ · 2H$_2$O were made to 250 ml with distilled water and filtered.

(B) 0.370 g of alizarin red S, C$_6$H$_4$(CO)$_2$C$_6$H$_4$(OH)$_2$SO$_3$Na, were dissolved in 250 ml of 2.10 N H$_2$SO$_4$.

Twenty-five ml of solution A were diluted with 100 ml of distilled water, 25.00 ml of solution B were added with stirring, followed by 500 ml of 2.10 N H$_2$SO$_4$ and sufficient distilled water to make a liter. This reagent was permitted to age 24 hours before using.

**Standard Fluoride Solutions.** A stock solution containing 100 µg (0.100 mg) F$^-$/ml was prepared by dissolving 222 mg of pure NaF (dried at 105° C) in water and diluting to a liter. A solution containing 10 µg F$^-$/ml was prepared by ten-fold dilution with water.

**Dilute Standard Fluoride Solutions.** Fluoride solutions ranging from 0 to 1.5 mg F$^-$/L were prepared in a synthetic sea water medium of chlorinity 17 °/oo unless otherwise specified. This is the chlorinity approximating the waters of Puget Sound and the Strait of Juan de Fuca. Synthetic media of this concentration were prepared from stock solutions made from NaCl and MgSO$_4$ · 7H$_2$O. The sodium chloride solution was made to contain 160 g/L and the magnesium sulfate solution 34.9 g MgSO$_4$ · 7H$_2$O per liter. These concentrations were verified through analysis for Cl$^-$ and SO$_4^{2-}$. One hundred ml of each of these solutions, when mixed and diluted to 500 ml with distilled water, gave a chloride and sulfate concentration corresponding to a sea water of chlorinity 19 °/oo; or, 89.47 ml of each of these solutions, when mixed and diluted to 500 ml with water, gave a chloride and sulfate concentration corresponding to a chlorinity of 17 °/oo.

**METHOD OF ANALYSIS**

Sea water samples of 50 ml volume were measured into 125 ml Erlenmeyer flasks. The alkalinity of each water sample was neutralized to pH 4 through the addition of a volume of acid which had been determined by acid titration of a separate 50 ml volume of sea water, using an appropriate acid-base indicator. Adjustment of the pH of the sample could also be done through acid titration, using a glass
electrode as indicator. Five ml of the reagent solution were added and the mixed solution was maintained at 28° C in a thermostat for six hours. The optical density of the solution was read in a Beckman DU spectrophotometer at a wavelength of 512 mµ using a 10 cm cell.

The optical density readings in this paper are reported in respect to distilled water reference solutions. Since greater accuracy could be attained in the lower range of transmissions by using a reference standard approximating the unknowns in optical density, a solution of cobaltous nitrate with an optical density of 0.242 was used for this purpose. Such a value is close to that given by the indicator in a solution of 17 °/oo chlorinity containing no fluoride. For routine analysis of sea water, a solution of optical density 0.140, near that obtained for 0.9 mg F⁻/L, would be more convenient and accurate.

**EXPERIMENTAL**

**Optical Density Curves at Various Wave Lengths.** Absorption at various wavelengths was measured on synthetic sea water samples, the results of which are shown in Fig. 1. Maxima were observed in

![Figure 1](image_url)

Figure 1. Absorption spectra of zirconium-alizarin sulfonate lakes in synthetic sea water solution, Cl = 17 °/oo. Curve A: Absorption spectra of lake with no fluoride present; Curve B: Absorption spectra of lake with 0.4 mg F⁻/L present; Curve C: Absorption spectra of lake with 0.8 mg F⁻/L present.
the curves at 418 and 512 m\(\mu\). The former is due to free alizarin sulfonate and the latter to the zirconium-alizarin sulfonate lake. With the addition of fluoride, the absorption at 418 m\(\mu\) increased because of the displacement and liberation of alizarin sulfonate from the lake by the fluoride, while at 512 m\(\mu\) the absorption decreased because of the destruction of the lake by the reaction of the fluoride with the zirconium. With sufficient fluoride the maximum at 512 m\(\mu\) disappeared. It is quite possible to estimate the fluoride content of the sample at either wavelength, and in the exploratory work the readings were taken at both wavelengths. Interfering substances have the same relative effect at either wavelength. Eventually the 512 m\(\mu\) wavelength was selected as the more desirable for the analysis because of the greater sensitivity to fluoride concentration at this wavelength.

Composition of the Zirconium-Alizarin Sulfonate Reagent. The composition and structure of the zirconium-alizarin red S reagent is not at all certain. From a spectrophotometric study of zirconium-alizarin lakes, Flagg, Liebhafsky and Winslow (3) concluded that the lakes are definite compounds, formed with a molar ratio of zirconium/alizarin of 1/1 and with the structure shown in formula I, regardless of whether they were formed from equivalent amounts of zirconium and alizarin or with one in excess. By analogy the zirconium-alizarin red S lake would have the formula shown in formula II.

![Formula I](image1)

![Formula II](image2)

On the other hand, Weiser and Porter (7), from their investigations, decided that lakes are not definite compounds at all but rather are held together by adsorption forces.

The zirconium-alizarin red S lakes to be used for fluoride reagents are prepared with the zirconium in large excess. In Lamar's reagent, zirconium is in excess, with a zirconium-alizarin red S ratio of 6.3. Since this reagent is prepared in a 1.1 N sulfuric acid solution, most of the zirconium excess would be complexed with sulfate ion forming \(\text{ZrSO}_4^{++}\), \(\text{Zr}\\(\text{SO}_4\)_2\), and \(\text{Zr}\\(\text{SO}_4\)_3^-\) (1).

The possibility of improving the sensitivity of the Lamar reagent
through change in composition led to experiments with varying ratios of zirconium/alizarin sulfonate. It was determined that the addition of 25% extra \( \text{ZrO(NO}_3\text{)}_2 \) to Lamar's indicator lessened the sensitivity of the indicator to fluoride and resulted in greater fluctuations with sulfate. Addition of 25% extra alizarin red S to the normal indicator gave slightly greater sensitivity to fluoride at moderate sulfate concentrations, but this resulted in considerable loss of linearity.

\[
\begin{array}{c|c|c|c|c|c|c|c|c|c|c}
\text{TIME (HOURS)} & 1 & 2 & 4 & 8 & 16 & 32 \\
\hline
0.075 \text{ MILLIGRAMS F}^-/L & \circ & \circ & \circ & \circ & \circ & \circ \\
0.100 \text{ MILLIGRAMS F}^-/L & \circ & \circ & \circ & \circ & \circ & \circ \\
0.125 \text{ MILLIGRAMS F}^-/L & \circ & \circ & \circ & \circ & \circ & \circ \\
0.150 \text{ MILLIGRAMS F}^-/L & \circ & \circ & \circ & \circ & \circ & \circ \\
0.175 \text{ MILLIGRAMS F}^-/L & \circ & \circ & \circ & \circ & \circ & \circ \\
0.200 \text{ MILLIGRAMS F}^-/L & \circ & \circ & \circ & \circ & \circ & \circ \\
0.225 \text{ MILLIGRAMS F}^-/L & \circ & \circ & \circ & \circ & \circ & \circ \\
0.250 \text{ MILLIGRAMS F}^-/L & \circ & \circ & \circ & \circ & \circ & \circ \\
0.275 \text{ MILLIGRAMS F}^-/L & \circ & \circ & \circ & \circ & \circ & \circ \\
\end{array}
\]

Figure 2. Effect of time upon the color development in synthetic sea water solution. \( \text{Cl} = 17\% \). Optical density observations at 512 mµ.
of fluoride response. Consequently Lamar's reagent was used unchanged in composition.

**Effect of Time on Color Development.** The development of color with time is shown in Figs. 2 and 3 for the wavelengths 420 and 512 mµ. It can be seen that no constant value is reached within any reasonable time. However, the variation after 4 or 5 hours is slight, and a 6-hour time for color development was selected as satisfactory from a standpoint of stability and convenience. A time variation of plus or minus an hour gave an error considerably less than the random error of the determination. At considerably greater times, such as 27 or 48 hours, there was loss in precision, so that longer times seemed undesirable.

![Figure 3](image_url)

*Figure 3. Effect of time upon the color development in synthetic sea water solution, Cl = 17 °/oo. Optical density observations at 420 mµ.*
The time of aging the indicator before its use is likewise important. Lamar recommended that the indicator stand at least an hour after its preparation before being used to insure equal development of standards and unknowns. Spectrophotometrically, since there are no comparison standards to compensate for changing sensitivity of the reagent, it is necessary to have an indicator sensitivity that is constant with time. It was found that spectrophotometrically the indicator attained a satisfactory constancy after an aging period of 24 hours.

Figure 4. Effect of temperature upon the color development at various fluoride concentrations. Synthetic sea water solution, Cl = 17 °/oo. Optical density observations at 512 mµ.
Freshly prepared indicator gave less lake color, which is interpreted as an apparent fluoride content higher than the true value. After the 24-hour aging period, the sensitivity changed but slowly, giving a result only about 1% low even after a month's standing under room conditions (in the dark).

**Effect of Temperature on Color Development.** Variation in temperature greatly changed the optical densities involved in this determination. The incubation temperature of 28°C for this work was selected because it was a convenient temperature slightly above room temperature. Fig. 4 illustrates the effect of a small increase in the incubation temperature. Reproducibility then demands a constancy in incubation temperature and sufficient rapidity in making the spectrophotometric measurements so that no appreciable temperature change takes place either by exchange of heat with the surroundings or by absorption of energy from the light passing through the sample.

**Effect of Light on Color Intensity.** From preliminary investigations it was thought that illumination during incubation changed the optical densities. This was disproved when it was found that the optical densities of samples exposed to 13 to 14 foot-candles of indirect illumination for the six-hour incubation period were unaffected. Of course, change in temperature due to absorption of light during incubation or measurement of the optical densities would affect the results, as mentioned previously.

**Effect of Volume of Solution on Color Intensity.** Experimentally it was found that 300 ml samples, for example, did not develop exactly the same optical density as 50 ml samples. This, possibly, was a surface effect, but it was not investigated at any length. It was avoided by taking the same volume and the same size flasks for all samples.

**Effect of Hydrogen-ion Concentration on Color Intensity.** Hydrogen ion has considerable effect on the optical densities observed, the effect being similar to that given by fluoride. For this reason the acid content of the indicator should be maintained at a constant level and the hydrogen-ion concentration of the samples should be adjusted. In determining this effect, samples of varying fluoride content were made 0.01 N in respect to hydrogen ion by the addition of 0.5 milli-equivalent H₂SO₄ to 50 ml of solution, and these were compared with a series of samples to which had been added an equivalent amount of magnesium sulfate to compensate for the sulfate effect. It can be concluded from these results, as shown in Fig. 5, that this concentration of hydrogen ion gave an apparent increase of 0.21 mg F⁻/L at a level of 1.2 mg F⁻/L. An identical experiment with HCl and NaCl gave essentially the same results.
Present in sea water are a number of anions of weak acids which react with hydrogen ion and buffer the solution. The ones in largest quantities are $\text{HCO}_3^-$, $\text{CO}_3^{2-}$ and $\text{H}_2\text{BO}_3^-$. The effect of these ions on the determination of fluoride is illustrated by the following experiments with $\text{HCO}_3^-$. Sodium bicarbonate was added to a series of

![Graph]

Figure 5. Effect of $\text{H}^+$ and $\text{SO}_4^{2-}$ upon the color development of various fluoride concentrations. Synthetic sea water solution, $\text{Cl} = 17\%$. Optical density observations at 512 $\text{m}$.$\mu$. 
samples to give a concentration of 250 mg HCO$_3^-$/L, which is equal to twice the amount expected in sea water of Cl = 17°/oo (5). The fluoride readings at 0.9 and 1.2 mg F$_{-}$/L were low by 0.13 mg and at 1.5 mg F$_{-}$/L they were low by 0.21 mg/L.

These results would indicate that the effect of the hydrogen ion is neither constant over a range of fluoride values nor linear with respect to the amount of acid added. Accordingly a good procedure for the determination of fluoride would avoid changes in acidity rather than attempt to apply a correction factor.

**Effect of Sulfate Interference.** Using Fig. 5, the effect of sulfate may also be determined by a comparison of the magnesium sulfate curve with a curve for a standard containing a normal amount of sulfate. At a level of 1.2 mg F$_{-}$/L this increase amounted to 0.05 mg/L. Since the SO$_4^{2-}$/Cl$^{-}$ ratio in sea water is nearly constant, correction for varying sulfate concentration may be most conveniently made by preparing calibration curves at different chlorinities. In Table I and Fig. 6 are shown data for chlorinities 15, 17, and 19°/oo. Below 0.9 mg F$_{-}$/L the sulfate effect, between chlorinities of 15 and 19°/oo, is less than the experimental error. At a fluoride level of 1.5 mg F$_{-}$/L, the effect between chlorinities of 15 and 19°/oo amounts to 0.05 mg F$_{-}$/L. The

![Figure 6. Effect of chlorinity upon the color development at various fluoride concentrations. Optical density observations at 512 m.$\mu$.](image-url)
sulfate effect as determined here for Lamar’s reagent is only about one-fifth that observed for Thompson and Taylor’s reagent. In many cases a single calibration curve for Cl = 17°/oo would be sufficient, but for maximum accuracy it would be desirable to know the chlorinity of the water and to use the appropriate calibration curve.

TABLE I. CALIBRATION DATA FOR VARYING CONCENTRATIONS OF FLUORIDE AT DIFFERENT CHLORINITIES

<table>
<thead>
<tr>
<th>Fluoride Content (mg/L)</th>
<th>Optical Densities</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cl = 15 °/oo</td>
</tr>
<tr>
<td>0</td>
<td>0.2475</td>
</tr>
<tr>
<td></td>
<td>0.248</td>
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<tr>
<td></td>
<td>0.250</td>
</tr>
<tr>
<td>0.9</td>
<td>0.139</td>
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<tr>
<td></td>
<td>0.139</td>
</tr>
<tr>
<td></td>
<td>0.1415</td>
</tr>
<tr>
<td>1.2</td>
<td>0.1075</td>
</tr>
<tr>
<td></td>
<td>0.1085</td>
</tr>
<tr>
<td></td>
<td>0.107</td>
</tr>
<tr>
<td>1.5</td>
<td>0.083</td>
</tr>
<tr>
<td></td>
<td>0.083</td>
</tr>
<tr>
<td></td>
<td>0.082</td>
</tr>
</tbody>
</table>

Average deviation of a single determination, Cl = 17 °/oo: 0.6 µg
Standard deviation of a single determination, Cl = 17 °/oo: 0.9 µg
Probable deviation of a single determination, Cl = 17 °/oo: 0.6 µg

Effect of Borate Interference. Borate is known to be present in sea water in considerable quantities. It was thought possible that borate might interfere with the fluoride determination through the formation of the fluoborate ion, BF₄⁻. Preliminary experiments with large amounts of borate indicated appreciable interference. With a borate concentration of 100 mg boric acid per liter, which is four times the amount occurring in sea water, a fluoride concentration low by about 0.03 mg F⁻/L was observed. This would mean that with a borate concentration equal to that in sea water the error would be within the experimental error.

Effect of Ferric Ion Interference. Similarly it was thought desirable to test for possible interference of the ferric ion through the formation of the fluoferrate ion, FeF₆³⁻. An iron concentration of 0.1 mg Fe³⁺/L, which is five times that present in sea water, was used to test its effect.
No interference was noted when the fluoride content was 1.5 mg/L, but high fluoride values were noted for the low concentrations, and in the case of the blank it amounted to 0.06 mg F⁻/L. This, of course, is just the opposite effect to that caused by the removal of fluoride through the formation of the fluoferrate. Since the iron concentration in the sea is only one-fifth of that used in this experiment, the interference would be within the limits of measurement, even if all the iron were available as ferric ion, which seems to be contrary to fact.

**Effect of Phosphate Interference.** Likewise using 5.4 mg Na₂HPO₄ · 12H₂O per liter, which is five times the maximum phosphate present in sea water, no effect was noted at a level of 1.2 mg F⁻/L, but the results were low by 0.02 mg F⁻/L at 0.9 mg F⁻/L and 0.07 mg F⁻/L with no fluoride present. At concentrations of phosphate normally present in sea water the interference would be negligible.

**Reproducibility of Results.** The precision of this determination may be ascertained from the results listed in Table I. The average deviation, standard deviation, and probable deviation for a single determination have been calculated for the series Cl = 17 °/oo (Table I). The probable deviation for a single determination corresponds to 0.0006 mg F⁻/L.

The deviation determined in Table I is quite a bit less than the 0.02-0.05 mg F⁻/L variation in the observations reported by Thompson and Taylor (6). This emphasizes the greater accuracy of measurement attained with the spectrophotometric method.

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