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ABSTRACT

Fluoride concentrations in complex natural waters, such as estuaries, rivers, or lakes, may be measured using an ion-selective electrode and a known-addition technique in conjunction with a complexing buffer. No additional information, such as interfering ion concentrations or ionic strength, is needed. Reliable measurements may be made in river waters containing as much as 25 mg/l Al^{3+}, 125 mg/l Fe^{3+}, 20 g/l Ca^{2+}, or 2.5 g/l Mg^{2+}. Results are accurate to about 0.02 mg F/l. In rivers, the relative standard deviation is 1% to 2% when the fluoride concentration is 1 mg/l and up to 5% when its concentration is 0.1 mg/l. In estuaries, the relative standard deviation ranges between 0.3% and 1.0% under typical conditions.

PROBLEM STATUS

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

AUTHORIZATION

NRL Problem G02-03
Project RR 104-03-41-5052

Manuscript submitted October 12, 1970.

DETERMINATION OF FLUORIDE POLLUTANTS IN NATURAL WATERS USING A KNOWN-ADDITION TECHNIQUE

INTRODUCTION

Fluorine is an important toxicant that must be monitored in the environment. A fluoride concentration of more than 1.2 to 1.5 mg/l in drinking water causes damage, while too little promotes dental caries. Fluorides are classified as highly toxic (Sax, 1963); they harm both plants and animals when introduced into the atmosphere as gases, mainly HF and SiF_4, and particulates or when injected into surface waters (McCune, 1969; Hunter, 1962; Shupe, 1969). High local concentrations can come from volcanic emanations, from industrial plants processing phosphate/rock/fertilizer, steel, aluminum, chemicals, coal/fuel oil, brick/tile/ceramics, and uranium (Carpenter, 1969; Hunter, 1962), and from feed supplements, insecticides, and rodenticides rich in fluorides (Shupe, 1969). Most local emissions of airborne fluoride quickly cause increased levels in nearby vegetation or surface waters, which then affect animal life. In one instance, surface waters 10 km from an industrial airborne source contained fluoride concentrations of 10.9 mg/l, and within a 5-km distance, trees, vegetables, fruit, bee colonies, and cattle were adversely affected, and children's blood showed decreased hemoglobin and increased erythrocyte levels (Marier, 1968).

To assess the extent and effects of fluorine pollution, measurements are needed in a wide range of media, such as air, water, plant and animal tissues, bones, minerals, and body fluids such as urine and blood. Fluoride analysis in complex solutions has been rather difficult until recently; the usual procedures required considerable manipulation to separate fluoride from interfering substances. Simpler techniques became possible (Crosby, 1968) with the recent invention of fluoride-selective electrodes, for such electrodes respond directly to free fluoride ion activity, even in the presence of large excesses of most other ions. They have been used for the determination of fluoride in a variety of materials, such as phosphate rocks (Edmond, 1969), bones (Singer and Armstrong, 1968), air and stack gas (Elfers and Decker, 1968), seawater (Warner, 1969a; Brewer, Spencer and Wilkniss, 1970), and potable waters (Frant and Ross, 1968; Light, Mannion, and Fletcher 1969).

Most measurements have used direct potentiometry. It is rapid and convenient, but the solution chemistry must be known or controlled if the total concentration is to be determined, since the electrode responds only to free ion activity. Any fluoride bound in complexes will not be detected, and the ionic strength of the standard must match that of the unknown so that the activity coefficients are the same. Many ingenious techniques have been developed in which the chemical compositions of samples and standards are closely matched or in which high-ionic-strength complexing buffers are used to free complexed fluoride and to fix the ionic strength of the sample at some known high value. Harwood (1969) showed that the buffer suggested by Frant and Ross (1968) was effective in low-ionic-strength river water if $[Al^{+3}]$ was low, but that significant interference occurred if aluminum was present at concentrations of 0.2/mg/l when the fluoride concentration was 1 mg/l. Using an improved buffer, with cyclohexanediamine tetraacetic acid as the trivalent ion complexing agent, he obtained 95% recovery in water containing 3 mg Al/l.

The generality of the complexing buffer approach is limited, however. Actual Al^{+3} must be known (or be known to be small) to assess the probable errors of potentiometric measurements, and these errors will become more important in untreated rivers, where F^- is lower. These techniques become increasingly difficult to apply when complexing ions are present in high and unknown amounts, or when the total ionic strength of the sample is appreciable. This is the situation in some polluted rivers and lakes, and particularly in estuaries and saline lakes.

The main ions in natural waters that complex fluoride ions are Ca^{+2}, Mg^{+2}, Al^{+3}, and Fe^{+3}. The divalent ions form weak complexes and the trivalent ions form very strong ones. In estuaries, the water is essentially seawater as diluted by river water (Carpenter, 1957). Magnesium is abundant, iron, aluminum, and calcium are low, $[F^-]$ is about 0.2 to 1.4 mg/l, and ionic strengths range up to 0.7. In rivers, calcium predominates over magnesium, and variable amounts of iron and aluminum are found. Typical values of iron and aluminum concentrations in rivers are 0.1 mg/l, and the highest concentrations encountered are unlikely to exceed 25 mg/l Fe and 10 mg/l Al. The concentration of dissolved F^- is about 0.1 to 0.2 mg/l, although certain exceptional values as high as 23 mg/l have been reported (Livingstone, 1963). Very wide variations are found in saline lakes.

In such solutions, considerable simplification can result by using a known-addition or spike technique (Garrels, 1967; Durst, 1969; Orion, 1969; Orion, 1970), and in some cases it may be the only feasible approach. In the known-addition method, the unknown sample itself becomes the chemical matrix for the standardizing sample. The ionic strength can be very high, and its value need not be known. Very high concentrations of ions that complex fluoride can be tolerated, and in most cases their identities need not be known. Accurate determinations are possible even when the majority of the fluoride is bound in complexes. Although Bock and Strecker (1968) and Baumann (1968) demonstrated the usefulness of spike methods in waters of different ionic strengths and containing various interfering ions, these methods have been little used to date in complex natural fluids. The purpose of this study was to devise a method of analysis based on known additions that would be generally useful down to 0.1 mg F/l in various natural waters, with no prior knowledge of chemical composition. The principles involved are general and apply to other ion-selective electrodes as well, and while this application is to natural waters, analogous techniques should prove useful for a wide range of aqueous solutions prepared from a number of sources.

THEORETICAL CONSIDERATIONS

If C_0 is the total concentration of the ion of interest in the unknown and C_Δ is the amount its concentration is increased by the spike, then according to the formulation of Orion (1969, 1970),

$$C_0 = C_\Delta (e^{\Delta E/S} - 1)^{-1}. \qquad (1)$$

where ΔE is the potential change observed on spiking and S, the response slope of the electrode, is the theoretically predicted RT/F for the fluoride electrode (Warner, 1969b). This equation assumes that (a) the change in total ionic strength upon addition of the spike can be neglected, (b) the fraction of the ion being measured that is free and uncomplexed remains essentially constant, and (c) electrode interferences are not present in amounts that will affect electrode response. If the concentration of the spike

solution is C_1 and the volume of test solution and added spike are V_0 and V_1, respectively, then

$$C_\Delta = \frac{C_1 V_1 - C_0 V_1}{V_0 + V_1} \tag{2}$$

or, to a good approximation when $C_1 \geq 100\ C_0$,

$$C_\Delta = \frac{C_1 V_1}{V_0 + V_1}. \tag{3}$$

In natural waters, assumptions (a) and (c) are fulfilled by using a high-ionic-strength buffer, keeping $V_1 < 0.01\ V_0$ and $C_\Delta \approx C_0$. In most solutions, assumption (b) is also justified. As is shown below, the degree to which it is justified depends on the amounts and kinds of complexing ions present.

Let ϕ be the fraction of the total fluoride present in free, uncomplexed form when in the presence of complexing ion M^{n+}, whose first concentration equilibrium constant K_c is

$$K_c = \frac{\left[MF^{(n-1)+}\right]}{[M^{n+}]\ [F^-]}. \tag{4}$$

Since

$$\phi = \frac{[F^-]}{[F^-] + \left[MF^{(n-1)+}\right]}, \tag{5}$$

then combining Eqs. (4) and (5) gives

$$\phi = \frac{1}{1 + K_c\ [M^{n+}]}. \tag{6}$$

When F^- ions are added in the spike, some must combine with M^{n+} ions, causing ϕ to increase. If ϕ increases by 1%, C_0 calculated by Eq. (1) will be 2% low under the stated conditions (Appendix A). Taking this value as an upper limit for error tolerable from a change in ϕ, solution conditions may be defined under which a spike technique can be used. If $K_c[M^{n+}] < 0.01$, then any decreases in $[M^{n+}]$ upon spiking cannot change ϕ more than 1%. If $K_c[M^{n+}] > 0.01$, two cases can arise. If $[M^{n+}] >> [F^-]$, then the addition of F^- will cause small changes in $[M^{n+}]$ and again $\Delta\phi < 1\%$. However, if $[M^{n+}] \approx [F^-] \approx 10^{-5}$M (for natural waters) and if $K_c[M^{n+}] > 0.01$, then $\Delta\phi$ can exceed 1%, but this requires that $K_c > 10^3$. For the fluoride case, then, large background concentrations of ions such as Mg^{2+} ($K_c = 18$ for $\mu = 0.5$) and Ca^{2+} ($K_c = 3$ for $\mu = 0.5$) will not cause appreciable error. The only ions that can interfere are the relatively few with $K_c > 10^3$, such as Al^{3+} and Fe^{3+}. These ions can be reduced to sufficiently low concentrations by using the complexing reagent suggested by Harwood (1969). In questionable cases, results may be checked using a double spike (Orion, 1970).

EXPERIMENTAL PROCEDURE

Apparatus

Potentials between an Orion 94-09 LaF_3 electrode and a saturated calomel electrode, thermostated at $25.0 \pm 0.1°C$, were measured with an Orion Model 801 pH meter. Filtered voltage was displayed with suppressed zero on a recorder, 5 mV full scale. Spikes ranging from 0.05 to 0.25 ml were added using a Manostat Digipet accurate to ± 0.001 ml.

Reagents

Fluoride standards were prepared by weight and diluted as necessary. The complexing buffer (TISAB IV) was a slight modification of that proposed by Harwood (1969). It was identical to the TISAB of Frant and Ross (1968) except that the sodium citrate was replaced by 5 g of 1, 2-cyclohexanediamine tetraacetic acid (CDTA) per liter of solution. Spike solutions were 10^{-2}M NaF for estuarine water and river water containing 50 μM F^- (1 mg/l) and 10^{-3}M NaF for river water containing 5 μM F^-.

$Mg(NO_3)_2$, $CaCl_2$, $FeCl_3$, and $Al_2(SO_4)_3 \cdot K_2SO_4 \cdot 24H_2O$ were added to aqueous NaF standards to make synthetic river waters. All reagents were fluoride-free except $CaCl_2$, whose fluoride content was determined by both the previously described method (Warner, 1969b) and by the spike technique discussed here. Simulated estuarine waters were similarly prepared in diluted seawaters whose fluoride concentrations were first determined using the potentiometric method previously described (Warner, 1969a). Because complexation reactions can be slow, waters were prepared at least 24 hours before use, and control samples were analyzed after storage up to 2 months. Synthetic river waters containing high iron concentrations were made sufficiently acidic to hold all iron in solution prior to TISAB IV addition; otherwise colloidal precipitates of iron hydroxide irreversibly removed fluoride from solution. In estuarine waters, the pH was not modified and iron was permitted to precipitate partially when added to simulate iron-rich water pouring into an estuary.

Method

Samples were mixed with TISAB IV in the ratio of 5 ml of sample to 1 ml of buffer, making available 2.9 millimoles of CDTA per liter of test sample. Complexation of interfering ions was rapid for all ions except Al^{+3}; for Al^{+3} the fraction complexed at 25°C was still changing after 2 hours, but was constant after 20 hours. Accordingly, all samples were mixed with buffer at least 20 hours before analysis. Usually, 25 ml of the mixtures was taken for analysis. Potentials before and after spiking ($C_s = C_0$) were measured after 15 minutes. If a steady-state potential was not achieved, the remaining increment was estimated from the voltage-time curve; estimates did not exceed 0.3 mV. Using Eq. (1), the total concentration of fluoride C_0 was computed from the known ΔE and C_s, using the values of C_0 C_s in Table 1.

For 5 μM F (0.1 mg/l) in synthetic river water, slow electrode response made measurements tedious at ΔE 18 mV. Smaller spikes were used (ΔE 4.8 mV), and a technique sacrificing accuracy for speed was adopted. Potential measurements were arbitrarily made 15 minutes after each change in solution composition, and the remaining increment to steady-state potential was estimated. Estimates were limited to 0.3 mV to avoid the introduction of personal bias, although true increments were always larger. This procedure consistently underestimated ΔE and all resulting values for C_0 were positively biased, but within acceptable limits. To a first approximation, the error

Table 1
Values of C_0 C_2 as a Function of ΔE at 25°C for Electrodes with Theoretical Monovalent Slope of $S = RT/F$*†

ΔE (mV)‡	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
1.0	25.19	22.86	20.91	19.27	17.85	16.63	15.56	14.62	13.78	13.03
2.0	12.35	11.74	11.18	10.68	10.21	9.784	9.389	9.023	8.684	8.368
3.0	8.073	7.797	7.539	7.296	7.067	6.851	6.648	6.455	6.273	6.100
4.0	5.935	5.779	5.630	5.488	5.353	5.223	5.100	4.981	4.868	4.759
5.0	4.654	4.554	4.457	4.364	4.275	4.189	4.106	4.025	3.948	3.873
6.0	3.801	3.731	3.664	3.598	3.535	3.473	3.414	3.356	3.300	3.246
7.0	3.193	3.141	3.091	3.043	3.996	2.950	2.905	2.861	2.819	2.777
8.0	2.737	2.698	2.659	2.622	2.586	2.550	2.515	2.481	2.448	2.415
9.0	2.386	2.353	2.322	2.292	2.263	2.235	2.207	2.180	2.153	2.127
10.0	2.101	2.076	2.052	2.027	2.004	1.981	1.958	1.936	1.914	1.892
11.0	1.871	1.850	1.830	1.810	1.790	1.771	1.752	1.734	1.715	1.697
12.0	1.680	1.662	1.645	1.628	1.612	1.596	1.580	1.564	1.548	1.533
13.0	1.518	1.503	1.489	1.475	1.460	1.447	1.433	1.419	1.406	1.393
14.0	1.380	1.367	1.355	1.343	1.330	1.319	1.307	1.295	1.284	1.272
15.0	1.261	1.250	1.239	1.228	1.218	1.207	1.197	1.187	1.177	1.167
16.0	1.157	1.148	1.138	1.129	1.119	1.110	1.101	1.092	1.083	1.075
17.0	1.066	1.057	1.049	1.041	1.032	1.024	1.016	1.008	1.001	0.993
18.0	0.985	0.978	0.970	0.963	0.955	0.948	0.941	0.934	0.927	0.920
19.0	0.913	0.906	0.900	0.893	0.887	0.880	0.874	0.867	0.861	0.855
20.0	0.849	0.843	0.837	0.831	0.825	0.819	0.813	0.808	0.802	0.796
21.0	0.791	0.785	0.780	0.774	0.769	0.764	0.759	0.753	0.748	0.743
22.0	0.738	0.733	0.728	0.723	0.719	0.714	0.709	0.704	0.700	0.695
23.0	0.691	0.686	0.682	0.677	0.673	0.668	0.664	0.660	0.656	0.651

* C_0 C_2 $= (e^{\Delta E/S} + 1)^{-1}$

† Corresponding values of C_0 C_2 for electrodes with theoretical divalent slope ($S = RT/2F$) can be found by doubling the observed ΔE and using the above table; similar proportioning allows its use with electrodes having experimentally determined slopes, or at other temperatures.

‡ The value of ΔE is the number in this column plus the number at the top of any particular column to the right.

Table 2
Fluoride Recovery in Simulated Estuarine Waters
Using a Spike Technique

Sample	Resulting Concentrations (millimole/liter)				Nominal F Concentrations (μM/l)	Mean Recovery (%)	Rel. Std. Deviation (individual) (%)	Number of Samples
	Mg	Ca	Al	Fe				
100% Seawater	54	10	4×10^{-4}	2×10^{-4}	71*	99.5	0.6	6
50% Seawater†	27	5	2×10^{-4}	1×10^{-4}	36	99.1	1.0	6
20% Seawater	11	2	8×10^{-5}	4×10^{-5}	14	101.9	0.3	6
50% Seawater plus Ca	27	60	2×10^{-4}	1×10^{-4}	36	101.6	1.3	4
20% Seawater plus Mg	21	2	8×10^{-5}	4×10^{-5}	14	101.3	0.5	4
50% Seawater plus Mg, Al, Fe	57	5	2×10^{-2}	2×10^{-2}	36	98.4	0.0	4
20% Seawater plus Mg, Al, Fe	57	2	2×10^{-2}	2×10^{-2}	14	102.2	1.2	4
50% Seawater plus Mg, Al, Fe	60	5	2×10^{-1}	1×10^{-1}	36‡	97.8	1.5	5
20% Seawater plus Mg, Al, Fe	60	2	2×10^{-1}	1×10^{-1}	14	100.3	0.7	4

*Three different natural seawaters were used, all with salinities near 34.9 ‰; 71 μM = 1.35 mg/l
†50% seawater is seawater diluted 1:1 with distilled water.
‡0.2 mM Al = 5 mg/l; 0.1 mM Fe = 6 mg/l.

in C_0 will be about equal to the negative percent error in E; e.g., if E is 10% low, C_0 will be about 10% high.

RESULTS AND DISCUSSION

Results of fluoride analyses obtained in seawater and simulated estuarine waters ranging in salinity from 7 to 35 °/oo are summarized in Table 2. Concentrations of interfering ions were selected well above those expected from mixing river waters with estuary waters. Because Mg^{2+} complexes much more F^- than Ca^{2+}, the former was the main divalent cation interference studied. No difference was observed for measurements made in synthetic and real seawaters, and only the results for real seawaters are reported.

Results in simulated river waters are shown in Tables 3 and 4. The concentrations of interfering ions studied were well above those normally encountered in natural waters, even when severely polluted. Since CDTA was only available to complex 2.9 millimoles per liter of trivalent ions, concentrations above that level resulted in no measurable F^-. It is probable that higher concentrations of CDTA would permit fluoride determinations in the presence of even larger amounts of interfering ions, but this has not been experimentally verified. Results in Table 3 are representative of high-fluoride waters or those in which fluoride has been increased by treatment. Results in Table 4 are typical for untreated rivers. The actual error to be expected is nearly the same in each water. A 2% error at the 50 μM level is 1 μM/l as is a 20% error at 5 μM/l.

In the high-fluoride waters, a significant error (of about 8%) is noted only for waters containing very high (0.5M) magnesium levels. In general, at 50 μM F^- in virtually any natural water, results should be accurate to 2%, and the relative standard deviation of an individual measurement will be 1 to 2%. At the 5 μM F^- level, using the rapid method described, results will be 5% to 30% high, and the relative standard deviation will range between 1% and 5%.

Table 3
Fluoride Recovery in Simulated River Waters Containing 50 μM/l (1 mg/l)

Ion and Concentration Added	Mean Recovery (and Uncertainty*) (%)
None	100.7 (0.9)
Al (III) 0.4 mM (about 10 mg/l)	98.7 (1.6)
1.0 mM	101.0 (2.2)
Fe (III) 0.4 mM (about 25 mg/l)	100.6 (0.4)
1.0 mM	102.2 (1.2)
2.0 mM	99.1 (1.9)
Ca (II) 100 mM (about 4000 mg/l)	99.9 (0.9)
500 mM	100.4 (0.4)
Mg (II) 100 mM (about 2500 mg/l)	103.7 (0.9)
500 mM	108.4 (1.3)
Synthetic river 1†	101.2 (1.7)
Synthetic river 2‡	101.2 (1.7)

*Uncertainty is the relative standard deviation of an individual measurement; four to eight samples were measured at each concentration.

† Synthetic river 1 contained 0.1 mM Al, 0.1 mM Fe, and 25 mM Mg.

‡ Synthetic river 2 contained 0.4 mM Al, 0.4 mM Fe, and 50 mM Mg.

Table 4
Fl ride Recovery in Simulated River Water Containing 5 .M/l (0.1 mg/l)

Int ering Ion Co entration	Mean Recovery (%)	Rel. Std. Deviation (individual) (%)	Number of Determinations
Jone	128	4.9	8
0.2 iM Al(III)	125	3.4	4
0.3 iM Fe(III)	106	1.3	4
50 M Ca(II)	111	1.0	4
5(M Mg(II)	114	2.8	4

esults indicate that large variations in total ionic strength do not interfere with the accu cy of such determinations. Very large concentrations of ions that form complexes w h low stability constants can be tolerated if a measurable amount of free fluoride re ains in solutic This technique offers a convenient way to determine the amount fluoride impurity present in other reagents, because commonly the impurity levels a highest in those salts whose cations form flu ride complexes. Similar techniques s uld allow an accurate determination of fluo ide levels in many other media such as lant and animal tissues or biological fluids.

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Appendix A

ERROR IN CALCULATED VALUE OF FLUORIDE CONCENTRATION IF THE FRACTION UNCOMPLEXED AFTER SPIKE ADDITION CHANGES BY 1%

In the original solution, the total measured potential E_1 is

$$E_1 = E_0 + S \ln(\phi C_0), \tag{A1}$$

where C_0 is the total concentration of fluoride present, ϕ is the fraction of that total fluoride present in free uncomplexed form, and E_0 is a constant representing the portion of the total potential due to reference electrodes and internal solutions and also includes the (unchanging) fluoride ion activity coefficient. The potential E_2 in the solution after spiking, if ϕ does not change and if $C_\Delta = C_0$, is

$$E_2 = E_0 + S \ln(\phi C_0 + \phi C_\Delta) \tag{A2}$$

and

$$\Delta E = E_2 - E_1 = S \ln 2. \tag{A3}$$

Hence, from Eq. (1)

$$\frac{C_0}{C_\Delta} = \frac{1}{2 - 1} = 1.000, \tag{A4}$$

which is correct. But if ϕ_2, the fraction actually free after spiking, is 1.01ϕ, then $E_2 = E_0 + S \ln 2.02\phi C_0$, $\Delta E = S \ln 2.02$, and C_0 would be calculated from Eq. (1) as

$$C_0 = 0.98\, C_\Delta; \tag{A5}$$

that is, the computed result would be 2% low.

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13. ABSTRACT

Fluoride concentrations in complex natural waters, such as estuaries, rivers, or lakes, may be measured using an ion-selective electrode and a known-addition technique in conjunction with a complexing buffer. No additional information, such as interfering ion concentrations or ionic strength, is needed. Reliable measurements may be made in river waters containing as much as 25 mg/l Al^{3+}, 125 mg/l Fe^{3+}, 20 g/l Ca^{2+}, or 2.5 g/l Mg^{2+}. Results are accurate to about 0.02 mg F/l. In rivers, the relative standard deviation is 1% to 2% when the fluoride concentration is 1 mg/l and up to 5% when its concentration is 0.1 mg/l. In estuaries, the relative standard deviation ranges between 0.3% and 1.0% under typical conditions.

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14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Fluoride pollution						
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The test originally used to determine amounts of fluoride impurities in the reagents was not sensitive enough to detect a small amount present in the $Mg(NO_3)_2$; hence, this compound was considered fluoride-free. Later measurements using the known-addition technique in the 2M $Mg(NO_3)_2$ originally used in sample preparations showed that there was 6.3×10^{-6} mole of fluoride per mole of $Mg(NO_3)_2$. Although Tables 2 and 4 are unaffected in Table 3 revise the recovery values for fluoride in 50 μM simulated river water to:

Ion and Concentration Added		Mean Recovery (and Uncertainty) (%)
Mg(II)	100 mM (about 2500 mg/1)	102.4 (0.9)
	500 mM	102.0 (1.3)

In Results and Discussion eliminate the first sentence of the third paragraph. In the Abstract, revise the third sentence to read: "Reliable measurements may be made in river waters containing as much as 25 mg/1 Al^{3+}, 125 mg/1 Fe^{3+}, 20 g/1 Ca^{2+}, or 12.5 g/a Mg^{2+}."