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Effect of Ionic Strength on the Absorbance in Aluminum-Tiron Complex

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Abstract

This experiment examines the influence of ionic strength up to equivalent of that of seawater on the absorption value of the aluminum-tiron complex. The study was carried out in distilled water, seawater and diluted seawater 2, 5, 10, 100 and 1000 times dilution. The result shows that the absorption in seawater is 1.2 times higher than in distilled water but for 10, 100 and 1000 times diluted seawater the values obtained are almost the same as in distilled water. Statistical evaluation shows that there is strong correlation between Al concentration and absorption in all solutions, hence the method can be applied to quantify mononuclear aluminum even in aqueous media with high ionic strength(0.69), so the method can be applied even for sea water.

Introduction

Aluminum is the most abundant element in the earth's crust making up approximately 7% of solid matter in the soil (Sposito et al., 1996). Determination of aluminum becomes very important both to scientist's interested in the toxicity of aluminum to the terrestrial and aquatic organisms and to those who study mineral weathering and mineral neoformation. During soil erosion, soil is weathered to the nearby river and finally to the ocean resulting into silt problem on the coastal reef. In nature aluminum has a single stable oxidation state (+ III) only and can be found as a tetrahedrally coordinated cation (ionic radius = 0.046nm) or octahedrally coordinated cation (ionic radius = 0.061nm) in coordination with oxygen (Sposito et al., 1996). The solution aluminum is highly hydrated, although the primary water shell can be displaced by strong electronegative ligands such as F^- . Mononuclear hydrolysis products have all been proposed to results from the successive deprotonation of coordinated water (Hus, 1977). The hydrolysis proceed spontaneously when aluminum salt is dissolved in water (Hem, 1968). The polynuclear aluminum species are transient, metastable intermediates in the precipitation of $Al(OH)_3$ because if partial neutralized solution is at true equilibrium, it should contain only mononuclear aluminum species and the stable solid phase (Hem, 1968).

Different species of aluminum do exist, the nature and distribution of these species can be a function of ionic strength, total aluminum concentration, the total OH added, pH value, temperature, the anion present and the reactive ligand (Smith, 1971). These forms of aluminum have different reactivity as well as toxicity, for example organic aluminum is less toxic than inorganic aluminum. The chemistry of aluminum is very complex due to the variety of forms in which aluminum exist. These forms have ranges of extractability in solution due to wide

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range in particle size, crystallinity, and ionic composition. In addition to the exchangeable aluminum that is bound to the soil by electric charge, each precipitate of aluminum has its own solubility product and equilibrium with soil. Therefore different techniques have been developed to measure the quantity of aluminum species such as total aluminum, reactive aluminum, mononuclear and polynuclear Al etc. Several analytical studies of aluminum have been made in freshwater but few in seawater, this is due to the fact that in seawater aluminum exist as trace element ranging between 0.5 to 5 μ g/l (Grasshoff et al., 1983).

Recently the problem of soil erosion of the acidic soil in which red soil is weathered to the nearby river and finally to the ocean has been reported in many areas all over the world especial in Okinawa (Kadomura et al., 1978 and Yamamoto, 1976). This soil is the major carrier of Al in the form of clay colloidal brought to the ocean (Sverdrup et al., 1966). Honjo (1978) found that 7% and 2% of the total particulate matter in atlantic and pacific ocean respectively were clay (Broecker and Peng, 1982). Therefore we need to have techniques for quantification of Al in solution with high ionic strength.

In 1967, Takao Yotsuyanagi, Katsumi Goto and Masaichi Nagayama found that tiron can react quickly with mononuclear aluminum to form stable dissolved Al-tiron complex with maximum wavelength at 310nm. The optimum pH value was 5.4. In their experiment they only examine the effect of ionic strength ranging from 0.14 to 0.35. Although the increasing of absorbency of Al-tiron complex with the increase in ionic strength was known, the precise study was not yet done in higher ionic strength which can accommodate ionic strength of seawater 0.69. The authors examined the effect of ionic strength until high ionic strength of seawater. Absorption is sensitive to changes in pH. Hence the analytical solutions were buffered with hexamethylenetetramine at pH 5.4. In comparing the absorption coefficient of distilled water to that of seawater the difference is negligible. Clark and James (1939) obtained same value of absorption coefficient for distilled water and pure sea water (Sverdrup et al., 1966).

Materials and Methods

Standard solution was prepared by using $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ reagent grade stabilized by 1ml of 1M HCl one day prior to test and stored in polyethylene bottle. All reagents are prepared, stored and mixed as prescribed by Yotsuyanagi et al. (1967). 0.314g of tiron was dissolved in 100ml distilled water and 140g of hexamethylenetetramine was dissolved in 1l distilled water then pH was adjusted to 5.4 by conc. HCl. Two ml of tiron solution was mixed well with 5ml hexamethylenetetramine buffer solution followed by 10ml of sample. The mixture was adjusted to 25ml by distilled water. Blank determinations were carried out for every solution and we used that as reference for absorption values. The absorption values were measured by spectrophotometer at 310nm. Seawater used was filtered by 5-C filter paper. The calibration curves were made for Al concentration ranging from 1 to 5ppm. Six replicates were performed for each aluminum concentration. In order to reflect field environment experiments were carried out on distilledwater, seawater, 2, 5, 10, 100 and 1000 times dilution of seawater, so as to include an ionic strength of aquatic solutions in which Al transported with red soil to the final destination. The average values were used to plot the graphs, standard deviation, confidence limit for 95% confidence were determined. Deviation of single measurement from the mean was calculated from calculated standard deviation and probability of deviation based on normal frequency distribution. Also the results were checked for their reliability for computing mean by using the criteria that " The result is sufficient discrepant for rejection if its deviation from arithmetic mean exceed twice the standard deviation (Kolthoff and Sandell, 1952).

Results and Discussion

The results were summarized in Fig. 1 in which all Aluminum calibration curves were plotted in same axis.

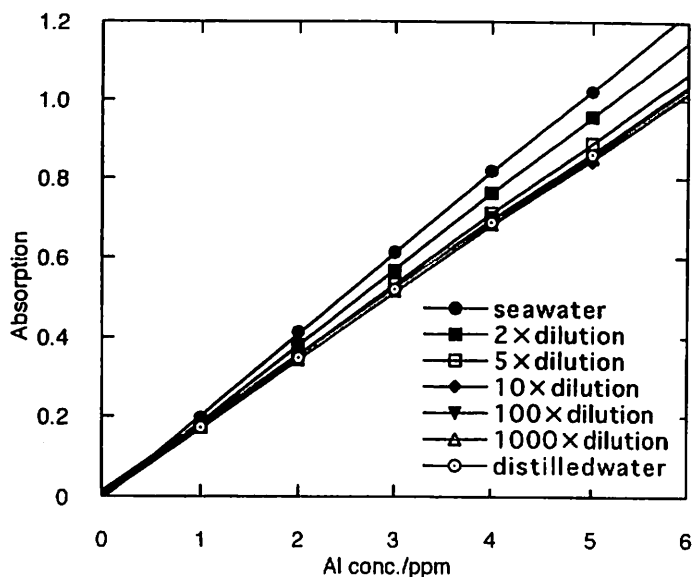
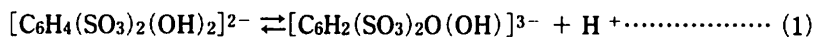


Fig. 1. Aluminum concentration vs absorption.

From Fig. 1 it shows that the absorption values are higher in seawater (ionic strength 0.69), but it decreases with increasing in dilution until 10 times dilution (ionic strength 0.069) the values are almost the same as in distilled water. Yotsuyanagi et al. (1967), had the same conclusion when they examined by using NaClO_4 for ionic strength from 0.14 to 0.35. This increase is due to increasing in dissociation of tiron at higher ionic strength as explained by the equation (Yotsuyanagi et al., 1967)



From Fig. 1 it shows that slope increases with increasing in ionic strength. The relation between slope with dilution was shown in Fig. 2. Also we can understand from Fig. 2 that the slope decreases with increasing in dilution until 10 times diluted seawater the slope is almost constant. This shows that the effect of ionic strength is negligible from 10 times diluted seawater.

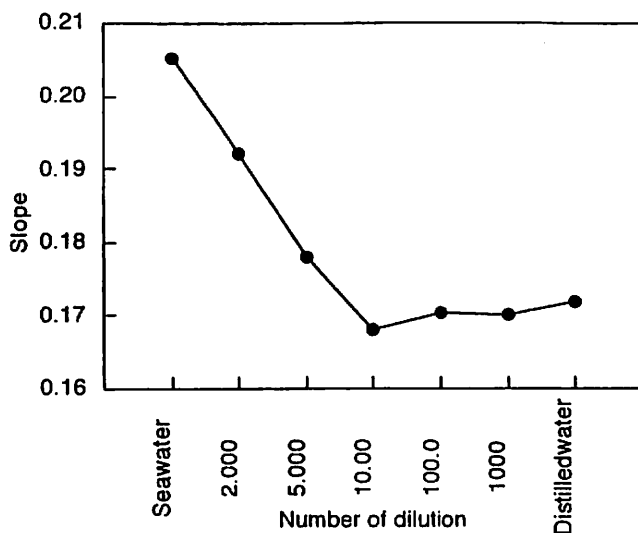


Fig. 2. Relation between dilution factor and slope.

The absorption is linearly related with concentration in all solutions as shown in Fig. 1 with $P < 0.0003$. This implies that the method can well express the relation between Al concentration and absorption even in seawater. The values of regression coefficient R are shown in Table 1.

Table 1. Slope and regression values.

Dilution ratio	Slope	R
Seawater	0.2051 ₃	0.9999 ₁
2.000	0.1921 ₀	0.9999 ₇
5.000	0.1778 ₇	0.9999 ₉
10.00	0.1681 ₃	0.9998 ₉
100.0	0.1704 ₂	0.9997 ₄
1000	0.1701 ₂	0.9999 ₈
Distilledwater	0.1718 ₇	0.9999 ₉

All absorption values used in computing mean values their differences from their corresponding arithmetic mean were less than twice of standard deviation, so they satisfy rejection criteria. The 95% confidence limits of the mean value were ± 0.00046 to ± 0.003 for distilled water, ± 0.007 to ± 0.001 for 1000 times diluted seawater, ± 0.008 to ± 0.003 for 100 times diluted seawater, ± 0.0009 to ± 0.005 for 10 times diluted seawater, ± 0.0008 to ± 0.002 for 5 times diluted seawater, ± 0.003 to ± 0.01 for 2 times diluted seawater and ± 0.004 to ± 0.01 for seawater. The standard deviations for six replicates were 0.0005 to 0.003 for distilled water, 0.0009 to 0.001 for 1000 times diluted seawater, 0.001 to 0.004 for 100 times diluted

seawater, 0.001 to 0.006 for 10 times diluted seawater, 0.001 to 0.003 for 5 times diluted seawater, 0.004 to 0.01 for 2 times diluted seawater and 0.006 to 0.1 for seawater, which means that the variations of data are small. The deviation of single measurement from the mean (\bar{X} -mean) was calculated by assuming probability of deviation as 0.046 for seawater and 2 times diluted seawater and 0.012 for the rest of the solution, even with that low probability [accepted significant probability of deviation is less than 0.05 (Kolthoff and Sandell, 1952)], but the deviation is still small. Therefore the result obtained in this experiment reflects the practical influence of salinity in aluminum measurement. The result shows that the accuracy of this method decreases with the increase in salinity. This could be due to the presence of other constituents in sea water like cations and organic ligand rather than ionic strength.

Conclusion

From this experimental result we conclude that tiron can be used for estimation of mononuclear aluminum species even in solution with ionic strength up to 0.69. The technique can be applied to estimate mononuclear aluminum even in sea water. Increase in ionic strength also increase in absorption value. The authors recommend further study with special emphasis on the extent of the effects caused by cation interference before it being used for speciation of Al in medium contain variety of ligands such as soil solution.

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