SYNTHESIS AND pH-METRIC DETERMINATION OF THE STABILITY CONSTANT OF IRON (III) PLANT-BASED OXALATO COMPLEX

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ABSTRACT

Calvin-Bjerrum's pH-metric titration technique, as modified by Irving and Rossoti, was used to determine the stability constant of synthesized iron (iii) plant-based oxalato complex in 50 % (v/v) ethanol-water solvent, at 300K and ionic strength of 0.1 M. Soluble oxalate was extracted from Spinacia Oleracea (Spinach) and the ligand, oxalic acid (as confirmed), was crystallized using sulphuric acid liberation method. The overall stability constant of the complex, logK was found to be 11.90 and the free energy, ΔG*, of the formation as* $-6.8359 \times 10^4 JK^{-1}mol^{-1}$*. The proton-ligand stability constants,* pK^H *calculated using half integral method at proton-ligand formation number,* $n_A = 0.5$ *and 1.5 are 1.50 and 4.40 for* pk_1^H *and* pK_2^H *respectively and 1.50 and 5.80 for point wise method. The stability constant of the complex shows that it is relatively stable. The negative free energy shows that the reaction for the formation of ferric oxalate is spontaneous, favouring the formation of the complex. With this result, it can be said that the consumption of half-boiled vegetables like Spinach may enhanced the formation of oxalate-related kidney stones which are serious health challenges nowadays since a stable complex can easily be formed.*

KEY WORDS: pH-metry, oxalato, stability constants, iron (iii) complex, kidney stones

INTRODUCTION

Kidney stone problems are one of global health challenges affecting people from 40 years and above[1]. Dietary oxalate is found in all plant foods with the amount of oxalate excreted in the urine considered an important risk factor in the development of calcium oxalate stones[2]. Research shows that 40-50% of urinary oxalate comes from the diet of healthy individuals consuming typical diets with 150-250 mg/d dietary oxalate[2]. Oxalic acid forms simple water-soluble coordination complexes in form of salts with K^+, Na^+ and NH_4^+ ions easily and insoluble oxalates complexes with Ca^{2+}, Fe^{2+} and

Mg^{2+} (making them unavailable for utilization in the body). It is sometimes difficult for the body to get rid of the insoluble oxalato-complexes when formed due to several metabolic factors. This complex, if stable in the body can increase the risk of kidney stones (whose main constituents contain mostly calcium oxalate)[1]. Understanding the stability of these complexes formed from plant-based oxalic acid is important in giving any advice on diet and kidney stones. This forms the basis for which this research is carried out.

Scientists in the past have used Calvin_Bjerrum pH-metric titration technique in determining the stability constant of metal complexes[3-5]. Other methods explored in the past included but not limited to the following: polarography, spectrophotometry[6-8], vibration spectroscopy, NMR. spectroscopy, Potentiometry[10-11], ESR. spectroscopy, colorimetry, solvent extraction, solubility measurements[12], viscometry, reaction kinetics, X-ray studies, coagulation studies, Mossbauer studies etc. The stability constants of complexes determine their applications in; ion-exchange resins[13], solvent extraction[14], nuclear fuel reprocessing[15], chelation chemistry[16-17]: e.t.c.

Stability Constant of Complexes

The stability of a complex determined its ease of conversion. As such, complexes are categorized mostly as either stable or unstable[17]. It is equilibrium constant for the formation of a complex in solution and shows the strength of the interactions between the ligand(s) and the metal ion(s)[19].

The term stability is specific and means that the complex exists under certain conditions as it may be quite stable to one reagent and decomposes readily in the presence of another. Depending on the purpose of studying, kinetic stability (lability and inertness) or thermodynamic stability (stable and unstable) of a complex may be considered or both.

Step-Wise and Overall Stability Constant

According to Bjerrum[20], the formation of a complex in solution takes place through the stepwise addition of the ligands to the metal ion. Thus the formation of the complex MLn will take place by the following ‘n’ consecutive steps.

$$M + L \leftrightarrows ML \quad K_1 = \frac{(ML)}{[M][L]} \quad - \quad (i)$$

$$ML \leftrightarrows ML_2 \quad K_2 = \frac{(ML_2)}{[ML][L]} \quad - \quad (ii)$$

$$ML_2 \leftrightarrows ML_3 \quad K_3 = \frac{(ML_3)}{[ML_2][L]} \quad - \quad (iii)$$

Thus

$$ML_{n-1} + L \leftrightarrows ML_n \quad K_n = \frac{(ML_n)}{[ML_{n-1}][L]} \quad - \qquad (iv)$$

Where M=central metal cation, L=Monodentate ligand, n=maximum co-ordination number for the metal ion M for the ligand….. The equilibrium constants, K_1, K_2, K_3, ...K_n are called stepwise stability constants.

The formation of the complex MLn may also be expressed by the following steps and equilibrium constants.

$$M + L \xrightarrow{B_1} ML, \ \beta = \frac{(ML)}{[M][L]} \quad - \qquad (v)$$

$$M + 2L \xrightarrow{B_2} ML_2, \ \beta_2 = \frac{(ML_2)}{[M][L]^2} \quad - \qquad (vi)$$

Thus

$$M + nL \xrightarrow{B_n} MLn, \ \beta_n = \frac{(MLn)}{[M][L]^n} - \qquad (vii)$$

$$\beta_n \quad = \sum_{n=1}^{n=n} K_n \quad - \quad - \quad - \qquad (viii)$$

The equilibrium constants, β_1, β_2, β_3, ... β_n are called overall formation or overall stability constants. βn is the nth overall (or cumulative) formation stability constants. The higher the value of stability constant for a complex ion, the greater will be its stability. Alternatively 1/k values sometimes are called instability constant. Stepwise stability constants are also expressed as $\log_{10}K_1$, $\log_{10}K_2$ - - - - - $\log_{10}K_n$ while the cumulative stability constant is expressed as $\log_{10}\beta_n$.

MATERIALS AND METHODS

a. Sampling and Preparation

Spinacia Oleracea (Spinach) was randomly sampled from Maza-market in Jos, North Central Nigeria, washed with distilled-deionized water and stored for use. All the chemicals and reagents used for this work were of laboratory standards and prepared according to standard analytical procedures.

b. Preparation of ligand (oxalic acid) from spinach (Spinacia Oleracea)

The spinach was cut into small pieces and 100g weighed and boiled with deionized water for 30mins. The boiled spinach was homogenized using a food processor (Blender), centrifuged and the liquid separated by decantation. Calcium chloride solution (0.5M) was added drop-wise with stirring until full precipitation occurred. This was filtered and washed with cold water severally and 10% H_2SO_4 added.

Excess $H_2SO_{4(aq)}$ was removed by heating the solution in a gas fume cupboard at about 100^{o}C for 10 minutes. The solution was kept in a refrigerator at about 0^{o}C for 2 days for crystallization of oxalic acid (as confirmed). The crystals were washed with ice-cold water and dried. The Postulated equations of reactions are shown below:

$$K_2C_2O_{4(aq)} + CaCl_{2(aq)} \longrightarrow CaC_2O_{4(s)} + 2KCl_{(aq)}$$

$$CaC_2O_{4(s)} + H_2SO_{4(aq)} \longrightarrow CaSO_{4(s)} + H_2C_2O_{4(aq)}$$

c. pH-Metry Titrations

Calvin-Bjerrum and Calvin-Wilson pH titration techniques were employed[20-22]. Three titrations were carried out: Free Acid titration (A); Acid-Ligand Titration (A+L): Acid-Ligand-Metal Titration (A+L+M). The pH-metry titration was carried out using sigma-27 DP digital pH-meter which reads from 0.00 to 14.00 in steps of 0.005 after being calibrated. The following solutions were prepared accordingly:

i. Free acid solution (A) (5ml of 0.02 $HNO_{3(aq)}$ + 1.5 ml of 0.02 M KNO_{3aq})

ii. Acid-ligand solution (A+L)(5 ml of 0.02M $HNO_{3(aq)}$ + 2.5 ml of 0.02 M $KNO_{3(aq)}$ + 5 ml 0.01 M $H_2C_2O_{4(aq)}$) and

iii. Acid-ligand-metal solution (A+L+M) (5 ml of 0.02 M $HNO_{3(aq)}$ + 5 ml 0.01 M $H_2C_2O_{4(aq)}$ + 1.67 ml 0.01M $Fe(NO_3)_{3(aq)}$).

The ligand was acidified with HNO_3 in a 50% ethanol-water medium and the ionic strength kept constant using $NaNO_3$. The solutions were titrated against standard sodium hydroxide[20-21]. The pH curves versus ml of base were plotted to obtain the free acid curve, acid-ligand curve and acid-ligand-metal curve (Figure 1). The proton-ligand stability constant (pKa) and ligand-metal stability constant (pK) were calculated using the Irving-Rossotti method[22].

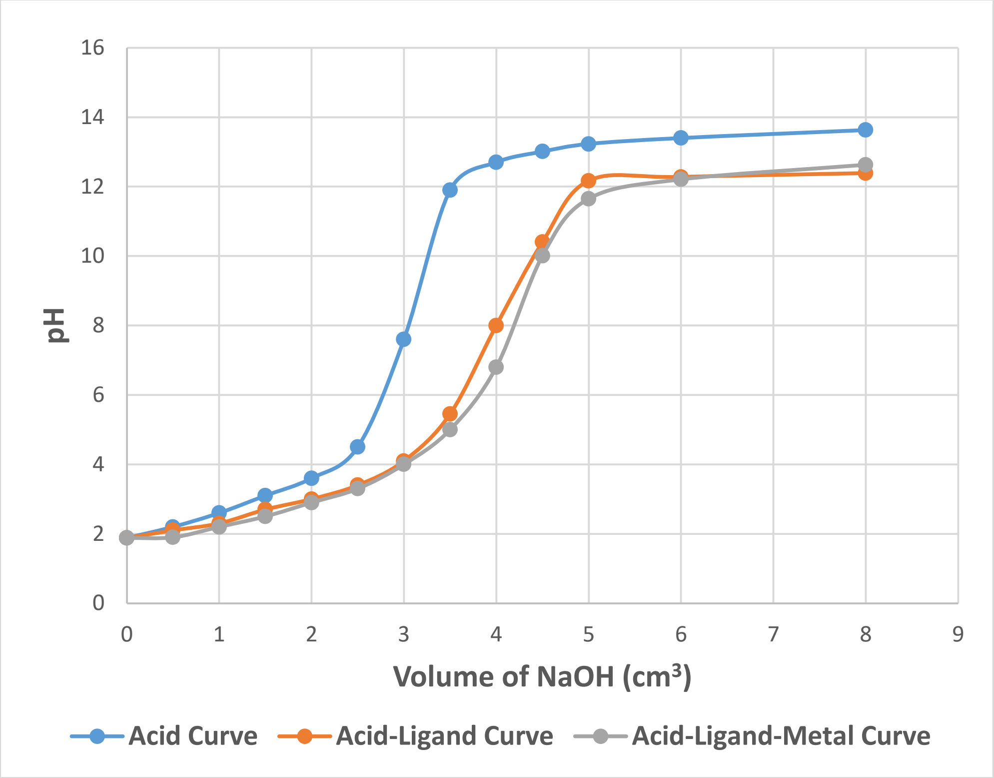

Figure 1: pH-metry curves

i. Proton-Ligand Formation Number, n_A at a given pH

This was obtained using the formular;

$$n_A = \gamma - \frac{(v_2 - v_1)(N - E^\circ)}{(v_0 + v_1)T_L^0}$$

Where;

γ= Number of replaceable hydrogen ions in the ligand=2

E°= Concentration of $HNO_{3(aq)}$= 4.27×10^{-3} M

V_0= Volume of solution=11.67 cm^3

V_1=Volume of alkali used during the A titration to yield a given pH

V_2= Volume of alkali used during A+L titration to give same pH as V_1

ii. Proton-Ligand Stability Constant, pK^H

Two methods were used:

a. Half Integral Method

The proton-ligand stability constants, pK^H, was calculated from the graph of pH against n_A using half integral method. The pK_1^H and pK_2^H values are the pH values when n_A are equal to 0.5 and 1.5 respectively.

b. Pointwise Method

For the calculations of pK_1^H, the expression below was used;

pK_1^H=log$\frac{nA-1}{2-nA}$+ pH (For n_A= 1.2 to 1.8)

And for pK_2^H,

pK_2^H= log $\frac{nA}{1-na}$ + pH (For n_A=0.2 to 0.8)

iii. Metal-Ligand Formation Number, n

The formular, n = $\frac{(v_3-v_2)(N+E°)}{(v_0+v_2)n_A\,T_M^0}$ was used.

Where;
v_3=Volume of alkali required to obtain the given pH with A+L+M mixture
T_M^0= Concentration of metal ion 1.453 × 10^{-3}M
n_A= The Proton-Ligand formation number for the given pH

iv. Free Ligand Concentration, pL

The formular used was; pL=-log[L]

The free ligand concentrations for each given pH were calculated using the following expression:

$$pL=\log\left[\frac{1+\left(\frac{H^+}{K_2^H}\right)+\left(\frac{H^{+2}}{K_1^H K_2^H}\right)}{T_L^0-T_M^0\,n}\times\frac{V^0+V_3}{V^0}\right]$$

Where:

K_1^H (7.4817 × 10^{-4}) and K_2^H(4.2150 × 10^{-10}) are the 1st and 2nd proton-Ligand stability constants respectively.
H^+ = Hydrogen ion concentration for the particular pH
V^0= initial volume of the solutions=11.7 cm^3
T_L^0= Total concentration of Ligand=4.27 × 10^{-3}M
T_M^0= Total concentration of metal ion=1.453 × 10^{-3}M
V_3=Volume of NaOH used to give the particular pH.
n = Metal-Ligand formation number at that particular pH.

v. Determination of Stability Constant, logK=β

a. Half-integral Method

i. A graph of n against pL was constructed to give the formation curve for the complex.
ii. The approximate values of log k_1, log k_2 and log k_3 (stepwise stability constants) were calculated from the formation curve by the known values of pL at which n= 0.5, 1.5 and 2.5 respectively.

b. Point-wise Method

The stepwise and overall stability constants was calculated using the data obtained.

logK_1 = pL + log $\frac{n}{1-n}$ (for n values between 0.2 to 0.8)

logK_2 = pL + log$\frac{n-1}{2-n}$ (for n values between 1.2 to 2.8)

logK_3 = pL + log$\frac{n-2}{3-n}$ (for n values between 2.2 to 2.8)

vi. Free Energy ΔG

The free energy was calculated using the expression;

$$-2.303RT\log K = \Delta G$$

RESULTS AND DISCUSSIONS.

The FTIR analysis results of the crystals (ligands) synthesized from spinach (Figure 2) shows peaks around 3437.27 cm^{-1}, 1666.55 cm^{-1} and 1095.60 cm^{-1}. These peaks are suspected to be hydroxyl group -OH), carbonyl group(C=O) and C-O group respectively. The peaks are similar to that of a pure carboxylic compound. The melting point of the plant based crystals was found to be $(190\text{–}196)^0$ C. These values are very close to the melting point of standard oxalic acid which is $(189\text{-}191)^0$ C. The difference can be due to the presence of impurities (e.g $CaSO_4$).

The plant-based ligand was used in the pH-metry titration after confirmation and the pH-metry curves (Figure1) were interpolated (Table 1). The values are used to determine the proton-ligand formation number at specific pH values. These were used to obtain the proton-ligand stability constant, pK^H, of the plant based ligand (Table 2). The pK_1^H and pK_2^H values obtained from half integral method are close to the values (1.46 and 4.40 respectively) reported by Clayton[23].

The metal ligand formation number and the free ligand concentrations at every given pH are shown in Table 3. These values are used to determine the stability constant of the complex, potassium ferric oxalate, using both the half integral and point-wise methods (Table 4).

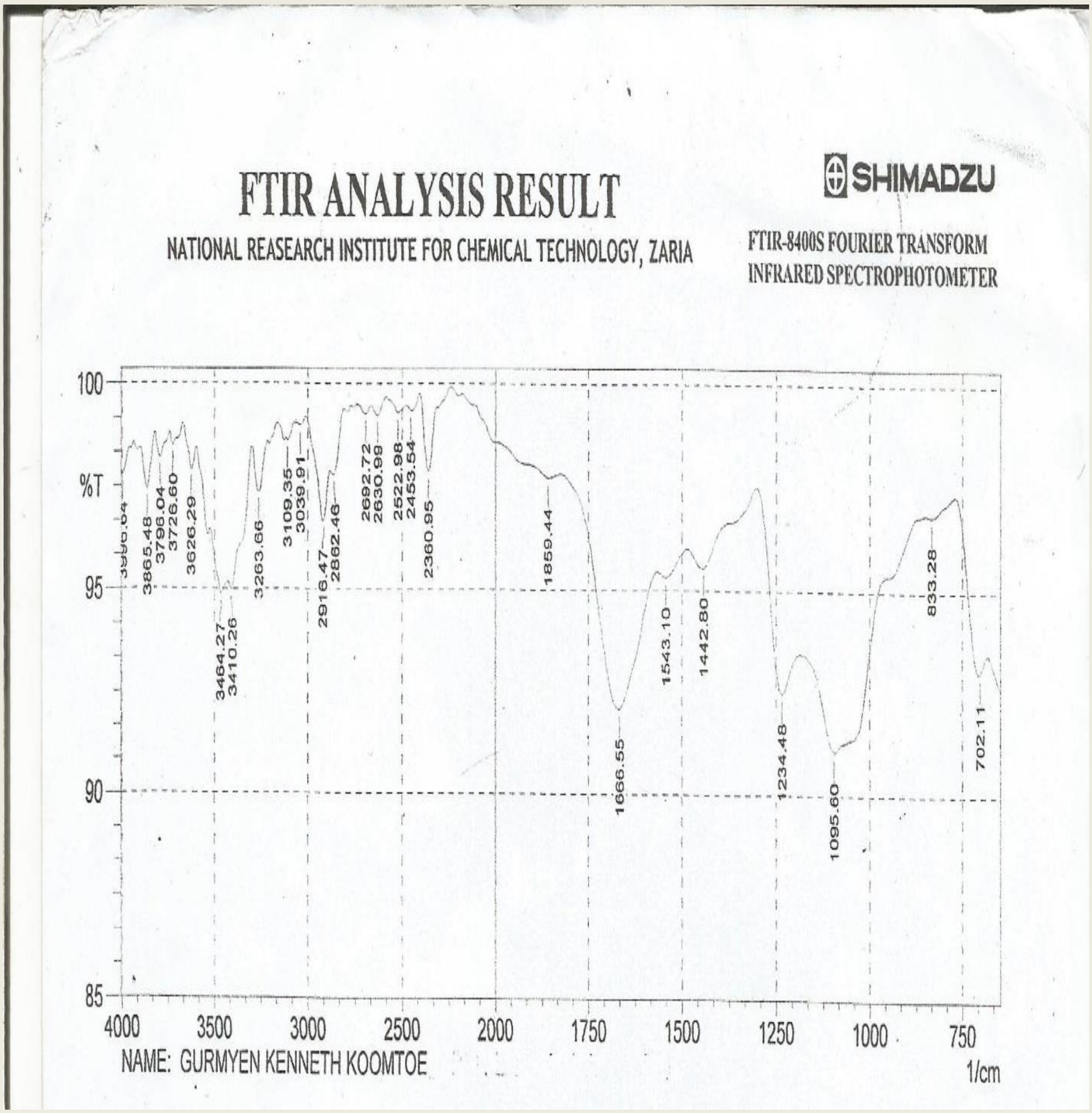

Figure 2: FTIR Spectrum for Plant-based Oxalate Crystals

Table 1: Interpolated Values from A, A+L, A+L+M Curves and the Proton-Ligand Formation Numbers, n_A for each Given pH.

pH	V_1	V_2	V_3	V_2-V_1	n_A
2.00	0.20	0.55	0.60	0.35	1.24
3.00	1.48	2.03	2.12	0.55	0.91
4.00	2.20	2.94	3.05	0.74	0.61
5.00	2.75	3.36	3.48	0.88	0.41
6.00	2.80	3.71	3.84	0.91	0.36
7.00	2.92	3.87	4.01	0.95	0.31
8.00	3.05	4.03	4.17	0.98	0.27
9.00	3.10	4.12	4.27	1.02	0.21
10.00	3.20	4.25	4.43	1.05	0.16

Table 2: Stepwise and overall proton-ligand stability constant

	$\mathbf{pK_1^H}$	$\mathrm{p}\mathbf{K_2^H}$	pK^H
Half-integral method	1.50	4.40	5.90
Point-wise method	1.50	5.80	7.30
Average	1.50	5.10	6.60

Table 3: Results for Metal-Ligand Formation Number, n_A, and the Free Ligand Concentration, pL, at given pH Values

pH	V_2	V_3	V_3-V_2	n	pL
2.00	0.55	0.60	0.05	0.2543	5.9773
3.00	2.03	2.12	0.09	0.5521	5.0032
4.00	2.94	3.05	0.11	0.9441	4.1131
5.00	3.36	3.48	0.29	1.4896	3.3789
6.00	3.71	3.84	0.32	1.7961	3.0129
7.00	3.87	4.01	0.38	2.2232	3.1234
8.00	4.03	4.17	0.42	2.5266	3.3566
9.00	4.12	4.27	0.53	3.6338	-
10.00	4.25	4.43	0.58	5.4062	-

Table 4: Stability constants of the complex

	$\log K_1$	$\log K_2$	$\log K_3$	$\log K(\beta_3)$
Half-Integral	5.15	3.35	3.40	11.90
Point-wise	5.30	3.60	2.99	11.89

From the results obtained, the two methods gave very close results, 11.90. The result for the stability constant of the complex shows that the complex is relatively stable under the conditions the research was carried out.

Free Energy, ΔG

The free energy, ΔG was calculated to be $\Delta G = -6.8359 \times 10^4$ J K^{-1} mol^{-1} from the equation $\Delta G = -2.303RT \log K$, signifying that the complexation reaction is spontaneous, favoring its formation.

CONCLUSION

Oxalic acid can be obtained from natural source like *Spinacia Oleracea* (Spinach) and the bidentate ligand, oxalato ($C_2O_4^{2-}$) used for the synthesis of coordination complexes of main and transition metals. The Metal-Ligand stability constant, logK, of the complex in 50% ethanol-water, at 27^{o} C and at ionic strength of 0.10 M was found to be 11.90. The results obtained using both point wise and half integral methods were found to be close. The free energy of the reaction is negative. This shows that the reaction is spontaneous favoring the formation of the complex. The results revealed that consuming high percentage of half-boiled vegetables pose kidney health risks due to the stable complex formed between the oxalate anion and metals such as iron, potassium, sodium and calcium which present in the body. Since the stability constant of this complex was not stated in available journals accessed during the time of this research, the result could be considered a baseline data (value) for the stability constant of the complex, whose high value (11.90) showed that it is very stable.

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