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STABILITY OF METALLIC IONS IN DILUTE SOLUTION*

By

Robert G. Milkey

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Trace Elements Investigations Report 373

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STABILITY OF METALLIC IONS IN DILUTE SOLUTION

By

Robert G. Milkey

ABSTRACT

Standard solutions and samples containing a few micrograms of metallic ion per milliliter are frequently used in trace-elements analysis. It is important to know whether the concentrations of such solutions remain constant from day to day. The stability of dilute solutions of three metallic ions--uranium, lead, and thorium--has been investigated.

The approximate pH of solutions that lost strength after standing for 2 1/2 months was determined, with the concentration of metallic ion varying from 1000 micrograms to 0.1 microgram per milliliter. Both adsorption and hydrolysis variously influenced the solute loss, but the minimum pH at which loss of concentration of lead and uranium occurred seemed to coincide with the pH at which the product of the hydrolysis of the metallic ion begins to precipitate.

The effect on stability of substituting polyethylene containers was investigated. No increase in stability was thereby obtained. It was further determined that the solutions which lost strength could not be restored promptly to the original concentration by some manual means such as shaking vigorously for several minutes.

INTRODUCTION

Part of a program undertaken by the Geological Survey, on behalf of the Division of Raw Materials of the Atomic Energy Commission, involves the chemical determination of trace amounts of uranium, lead, and thorium. The sample may be a natural water that is itself a very dilute solution of the metal ion. Also, very dilute standard solutions are often prepared for use in constructing standard curves.

The question arises as to the stability of these solutions. It is possible that their strength may change overnight. Of corollary importance is the type of container used to hold the solution. A solution stored in glass might suffer a greater loss in concentration than it would if stored in a container made of different material such as plastic--polyethylene.

The scope of the research embraces three objectives:

1. To determine the effect of the metal ion concentration on the stability of dilute solutions of a metal.
2. To determine the effect of the hydrogen ion concentration on the stability of dilute solutions of a metal.
3. To determine the relative stability of solutions stored in Pyrex and in polyethylene bottles.

DISCUSSION OF THEORY

The three principal factors that cause a change in the concentration of the solutions are hydrolysis, adsorption, and ion exchange.

Hydrolysis and precipitation of the metal ion

The hydrous oxide of the metal will theoretically precipitate when the solubility product has been exceeded. Thus, the relationship between the acidity of the solution and the amount of metal remaining in solution can be expressed, for the metal with valence n

$$K_w \sqrt[n]{\frac{[M^{+n}]}{P}} = [H^+]$$

where K_w = the ionization constant for water, 10^{-14}

M = the equilibrium concentration of the metal ion

P = the solubility product of the metal hydroxide

This relationship would hold whenever the hydroxide is present as the solid phase.

It is possible, however, for hydrolysis to occur without attendant precipitation, and then the solute would probably be present as aggregates distributed uniformly throughout the solution as a colloid. Usually such a colloid would be positively charged.

If such a colloid is formed, it is uncertain whether or not an analysis of the solution would indicate a change of concentration. The molecular aggregates may possess such high stability that they could resist chemical reaction with the reagent used to analyze the solutions.

Adsorption on walls of container

A gas or solute in solution brought in contact with a solid substance has a tendency to collect on the surface of the solid. This adsorption may be of two different types: chemical adsorption (chemisorption), and physical (Van der Waal's) adsorption.

The forces active in holding adsorbed molecules by means of chemisorption seem to be of the same order as the forces present in holding atoms together in the solid crystal. In both cases the activation energies are much the same. Like formation of compounds, chemisorption is characterized by strong bonding forces and depends on the chemical nature of both the surface and of the solute being adsorbed.

Van der Waal's adsorption, on the other hand, is attributed to the stray fields of force of the surface molecules which arise from their dipole nature. The forces active in such physical adsorption seem to be similar to those that cause gaseous molecules to coalesce and form a liquid. The physical bonding forces are much weaker than the forces of chemisorption and vary with the reciprocal of r^9, where r is the distance between molecules. Similarly the heat evolved is much smaller than that evolved in chemisorption, being of the same order of magnitude as the heats of liquification of gases.

The extent to which the adsorption will take place depends, therefore, on such factors as concentration of solute, nature of the solvent, size and valence of adsorbed ion, and dissociability of the adsorption complex.

Ionic exchange

This adsorption is characterized by the removal of some ion from the surface lattice and its replacement by an ion from the solution.

A clean glass surface is assumed to consist of a network of ions such as Si-O-Si and also Si-O-Na or similar groups. The effect of acid on the glass is to convert groups of the Si-O-Na to hydrated Si-OH groups, and the presence in solution of suitable ions will result in their exchange with the Na in the lattice.

The extent is usually governed by some relationship such as:

$$\frac{\text{Concentration of newly adsorbed ion on surface}}{\text{Concentration of newly adsorbed ion in solution}} = K\left[\frac{\text{Concentration of newly adsorbed ion on surface}}{\text{Concentration of newly adsorbed ion in solution}}\right]$$

where K is the distribution coefficient of the newly adsorbed ion between solution and surface.

By preparing various metallic ion solutions with different acidities and concentrations and allowing them to stand undisturbed for several months, a measurement of their metal concentrations at the end of that time should indicate which factors are instrumental in effecting their loss of strength.

ANALYTICAL PROCEDURE

Preparation of solutions

For each of three metals--uranium, thorium, and lead--a stock solution was prepared from the nitrate salts, containing 10 mg of metal per milliliter of solution. By successive dilutions of the stock solutions, the following solutions were prepared:

Uranium solutions

Solutions containing	With pH values
1000 micrograms/ml	0 1 2 3 4.5 4.74
100 micrograms/ml	0 1 2 3 4.5 4.82
10 micrograms/ml	0 1 2 3 4.6 5.4
1 microgram/ml	0 1 2 3 4.6 6.1
0.1 microgram/ml	0 1 2 3 3.76 4.82 6.6

Lead solutions

Solutions containing	With pH values
1000 micrograms/ml	0 1 2 3 3.7 5.25 5.7
100 micrograms/ml	0 1 2 3 4.5
10 micrograms/ml	0 1 2 3 5.0 5.3
1 microgram/ml	0 1 2 3 6.0 6.3
0.1 microgram/ml	0 1 2 3 5.11 6.4 7.1

Thorium solutions

Solutions containing	With pH values
1000 micrograms/ml	0 1 2 3 3.5 4.20
100 micrograms/ml	0 1 2 3 4.2
10 micrograms/ml	0 1 2 3 5.1
1 microgram/ml	0 1 2 3 5.7 6.4
0.1 microgram/ml	0 1 2 3 3.43 8.1

Each solution was divided into two parts; one part was placed in a Pyrex glass bottle, and the other part was placed in a polyethylene bottle. The bottles were tightly stoppered. The stoppers were further sealed with pliofilm. The solutions were allowed to stand for approximately 2 1/2 months.

Analysis of metal content

The uranium in all solutions and in the stock solution was determined fluorimetrically (Grimaldi and Levine, 1950).

Lead was determined by the dithizone method (Milkey, 1952).

For solutions containing 1000γ, 100γ, and 10γ of thorium per milliliter, the thorium was determined using sodium alizarin sulfonate. The pH of a suitable aliquot was adjusted with dilute NH_4OH to approximately 3.5. Three milliliters of formic acid-sodium formate buffer was then added. One milliliter of sodium alizarin sulfonate (0.0855 g/liter) was added, and the solution made to a volume of 25 ml. The optical density of the solution was determined at a wavelength of 540 mμ and slit width of 0.03 mm.

For solutions containing 1γ and 0.1γ thorium per milliliter, thorium was determined colorimetrically with 1-(o-arsonophenylazo)-2-naphthol-3,6-disulfonic acid (Thomason et al., 1949).

Figures 1, 2, and 3 show the percent of original concentration remaining after the solutions stood for approximately 2 1/2 months.

Table 1 shows which solutions exhibited a significant change in concentration, the initial and final pH values, the percent of original concentration remaining after standing, and the strength of solutions tested after one minute's vigorous shaking. A range of ± 7 percent in results was attributed to the allowable experimental error of the

Table 1.--Solution of metallic ions which diminished in concentration after standing for about two months.

Solution	Original concentration in γ/ml	Container	pH		Percent original concentration	
			Initial	Final	After standing	After shaking
			Uranium			
A	1000	Pyrex	4.5	4.4	87	93
B	1000	Polyethylene	4.5	4.3	62	70
C	1000	Pyrex	4.82	4.72	54	
D	1000	Polyethylene	4.74	4.65	55	
E	1	Pyrex	6.0	5.9	78	87
F	1	Polyethylene	6.2	5.5	76	81
G	0.1	Polyethylene	4.74	4.50	91	
H	0.1	Pyrex	6.7	3.8	82	92
I	0.1	Polyethylene	6.5	6.1	52	55
			Lead			
A	1000	Pyrex	5.7	5.60	71.5	
B	1000	Polyethylene	5.72	5.54	69.8	
C	1	Polyethylene	6.3	5.6	88	
D	0.1	Pyrex	6.4	6.3	39	49
E	0.1	Polyethylene	6.4	3.8	34	31
F	0.1	Pyrex	7.1	6.1	40	57
G	0.1	Polyethylene	7.1	6.0	18	33
			Thorium			
A	100	Pyrex	4.2	3.7	39	42
B	100	Polyethylene	4.2	3.7	36	
C	10	Pyrex	5.1	5.4	85	90
D	10	Polyethylene	5.1	5.0	80	83
E	1	Pyrex	5.7	4.8	37	39
F	1	Polyethylene	5.7	5.7	30	25
G	1	Pyrex	6.4	6.1	22	49
H	1	Polyethylene	6.4	3.5	25	28
I	0.1	Pyrex	3.43	3.42	50	
J	0.1	Polyethylene	3.43	3.35	30	
K	0.1	Pyrex	8.1	8.1	39	45
L	0.1	Polyethylene	8.1	7.2	39	33

fluorimetric and colorimetric methods.

DISCUSSION OF RESULTS

Effect of acidity and metal concentration

Uranium.--Conductivity experiments have shown that the product of the hydrolysis of uranium begins to precipitate at a pH of about 4.2. All uranium solutions which lost strength had a pH value of 4.3 or greater. No uranium solutions with pH of less than 4.2 decreased significantly in concentration, despite a range of uranium concentration from 1000 γ/ml to 0.1 γ/ml. Moreover, nine uranium solutions, with uranium ion concentration ranging from 100 γ/ml to 0.1 γ/ml and all with pH values greater than 4.2, did not show significant changes in concentration. Probably the presence of dissolved CO_2 in these solutions had an effect in inhibiting the precipitation.

Lead.--Conductivity experiments have shown that for moderate concentration of the nitrate solution, the product of the hydrolysis of lead begins to precipitate at a pH of 5.6 to 6.0. All lead solutions that lost strength had pH values of 5.6 or greater. No solutions with initial pH of less than 5.7 decreased significantly in concentration, despite a range of Pb^{++} concentration from 1000 γ/ml to 0.1 γ/ml. Moreover, three solutions with initial pH values of 6.0 or greater also did not decrease significantly in concentration.

Thorium.--Conductivity experiments have shown that the product of hydrolysis of thorium begins to precipitate at a pH of about 3.7. No thorium solutions with pH of 3.0 or less showed loss of strength. All thorium solutions with pH values of 3.7 or greater showed significant loss in concentration. Although solutions containing 1000 γ/ml at pH of 3.7 showed no change in concentration, preliminary experiments indicate that when the Th^{4+} concentration is as low as 0.1 γ/ml, appreciable losses occur at pH of about 3.4.

Calculation of solubility product

As the product $\left[M^{+n}\right]\left[OH^{-}\right]^{n}$ is equivalent to the solubility product, a series of values for each metal can be obtained using the final pH and the final solute concentration of the solutions. An inspection of the values thus obtained should help to indicate the extent to which hydrolysis and/or adsorption influenced the changes in concentration.

For lead, the relationship can be expressed as:

$$\frac{\left[Pb^{++}\right](K_w)^2}{\left[H^+\right]^2} = \text{solubility product}$$

where $K_w = 10^{-14}$

For uranium, the equation becomes

$$\frac{\left[UO_2^{++}\right](K_w)^2}{\left[H^+\right]^2} = \text{solubility product}$$

and for thorium,

$$\frac{\left[Th^{4+}\right](K_w)^4}{\left[H^+\right]^4} = \text{solubility product}$$

The calculated values are listed in table 2. Column 7 lists the equilibrium concentrations of the metal in each solution that results from the calculations using the values of solubility products presented in the literature. The published value of the solubility product of lead hydroxide is given as 1.35×10^{-15} by Britton (1942). Latimer (1952) gives the value 2×10^{-23} for uranyl hydroxide, and for thorium hydroxide 1.0×10^{-39}.

Table 2.--Solubility products of the metallic ion solutions which diminished in concentration after standing.

Sol.	Concentration Initial γ/ml	Concentration Initial Mols/liter (1)	Concentration Final Mols/liter (2)	Percent of initial concentration remaining (3)	pH Initial (4)	pH Final (5)	Calculated solubility products (6)	Calculated equilibrium concentration 1/ (7)	Container (8)
				Uranium					
A	1000	4.2×10^{-3}	2.27×10^{-3}	54	4.82	4.3	9.08×10^{-23}	5×10^{-4}	Pyrex
B	1000	4.2×10^{-3}	2.30×10^{-3}	55	4.74	4.3	1×10^{-22}	5×10^{-4}	Polyethylene
C	1000	4.2×10^{-3}	3.66×10^{-3}	87	4.5	4.4	3.66×10^{-22}	2.0×10^{-4}	Pyrex
D	1000	4.2×10^{-3}	2.61×10^{-3}	62	4.5	4.3	1.04×10^{-22}	5×10^{-4}	Polyethylene
E	1	4.2×10^{-6}	3.28×10^{-6}	78	6.0	5.9	2.06×10^{-22}	3.18×10^{-7}	Pyrex
F	1	4.2×10^{-6}	3.19×10^{-6}	76	6.2	5.5	3.2×10^{-23}	2.0×10^{-6}	Polyethylene
G	0.1	4.2×10^{-7}	3.82×10^{-7}	91	4.74	4.50	3.82×10^{-26}	2×10^{-4}	Polyethylene
H	0.1	4.2×10^{-7}	3.49×10^{-7}	82	6.7	3.8	1.38×10^{-27}	5.05×10^{-3}	Pyrex
I	0.1	4.2×10^{-7}	2.19×10^{-7}	52	6.5	6.1	3.48×10^{-23}	1.26×10^{-7}	Polyethylene
				Lead					
A	1000	4.84×10^{-3}	3.46×10^{-3}	71.5	5.7	5.6	5.48×10^{-20}	85	Pyrex
B	1000	4.84×10^{-3}	3.38×10^{-3}	69.8	5.72	5.54	4.0×10^{-20}	113	Polyethylene
C	1	4.84×10^{-6}	4.25×10^{-6}	88	6.3	5.6	6.74×10^{-22}	85	Polyethylene
D	0.1	4.84×10^{-7}	1.89×10^{-7}	39	6.4	6.3	7.54×10^{-23}	3.4	Pyrex
E	0.1	4.84×10^{-7}	1.65×10^{-7}	34	6.4	3.8	6.54×10^{-28}	3.42×10^{5}	Polyethylene
F	0.1	4.84×10^{-7}	1.94×10^{-7}	40	7.1	6.1	3.08×10^{-23}	8.5	Pyrex
G	0.1	4.84×10^{-7}	8.74×10^{-8}	18	7.1	6.0	8.74×10^{-24}	13.5	Polyethylene
				Thorium					
A	100	4.31×10^{-4}	1.68×10^{-4}	39	4.2	3.7	1.05×10^{-45}	1.6×10^{2}	Pyrex
B	100	4.31×10^{-4}	1.55×10^{-4}	36	4.2	3.7	9.70×10^{-46}	$1.6 \times 10^{+2}$	Polyethylene
C	10	4.31×10^{-5}	3.67×10^{-5}	85	5.1	5.4	1.46×10^{-39}	2.52×10^{-5}	Pyrex
D	10	4.31×10^{-5}	3.45×10^{-5}	80	5.1	5.0	3.45×10^{-41}	1×10^{-3}	Polyethylene
E	1	4.31×10^{-6}	1.60×10^{-6}	37	5.7	4.8	2.5×10^{-43}	6.35×10^{-3}	Pyrex
F	1	4.31×10^{-6}	1.30×10^{-6}	30	5.7	5.7	8.12×10^{-40}	1.6×10^{-6}	Polyethylene
G	1	4.31×10^{-6}	9.5×10^{-7}	22	6.4	6.1	2.39×10^{-39}	3.97×10^{-6}	Pyrex
H	1	4.31×10^{-6}	1.08×10^{-6}	25	6.4	3.5	1.08×10^{-48}	1×10^{3}	Polyethylene
I	0.1	4.31×10^{-7}	2.18×10^{-7}	50.5	3.43	3.42	1.03×10^{-49}	2.09×10^{3}	Pyrex
J	0.1	4.31×10^{-7}	1.3×10^{-7}	30.2	3.43	3.35	3.27×10^{-50}	3.9×10^{3}	Polyethylene
K	0.1	4.31×10^{-7}	1.68×10^{-7}	39	8.1	8.1	4.23×10^{-31}	3.97×10^{-16}	Pyrex
L	0.1	4.31×10^{-7}	1.68×10^{-7}	39	8.1	7.2	1.05×10^{-34}	1.58×10^{-12}	Polyethylene

1/ Published values for solubility products: $Pb(OH)_2$ 1.35×10^{-15}; $UO_2(OH)_2$ 2×10^{-23}; $Th(OH)_4$ 1.0×10^{-39}.

Considering the values in table 2, one must take into account certain factors inherent in the analyses:

1. There is possibility of error in the measuring of pH in the range 4.5 to 7+ because solutions are not buffered. The calculation of the solubility product of thorium would be particularly affected as the hydroxyl ion concentration is raised to the fourth power.

2. The presence of a "salt effect" in the most concentrated solutions could affect the solubility products.

3. In the calculation of the solubility products and of the metal solute concentration at equilibrium no account was taken of the possible formation of basic salts. For each metal solute a whole series of basic salts is possible (Britton, 1925) in which the anions are made up of (OH^-) and (NO^-_3) in varying ratios to each other. It is also possible that these salts may be somewhat soluble. Thus, neutralization experiments have shown that when a solution of NaOH is added slowly to a dilute thorium solution, the ratio of thorium to the equivalents of (OH^-) necessary for complete precipitation of thorium is 1:3.24. This corresponds to a hydrolytic precipitate of $Th(OH)_{3.24}(NO_3)_{0.76}$. Recalculating the solubility product of the first thorium solution on this basis alters the figure from 1.05×10^{-45} to 2.18×10^{-38}.

It will be noted that uranium solution H, lead solution E, and thorium solution H exhibited particularly large changes in pH after standing. Part of the change can be attributed to hydrolation of aqua groups, but there is no obvious reason why the change should be greater than was found for comparable solutions.

Table 3 shows that the calculated values for the solubility products of the three solutions were far out of line with the others. However, when the products are recalculated using the initial instead of the final pH of the solutions, they agree reasonably well with the solubility products of comparable solutions.

CONCLUSIONS

A consideration of all of the above factors leads to the following conclusions:

An inspection of columns 7 and 2 in table 2 shows that the final concentrations of lead in each of the solutions which lost strength is far short of the concentration necessary to precipitate the hydroxide. However, a detectable amount of fine white precipitate was present in solutions A and B. This would indicate the precipitation of a double salt of lead in these two solutions. Researchers (Britton, 1925) have, for example, obtained the mixed salt of formula $Pb(NO_3)_2$, $3Pb(OH)_2$, with solubility product of the order of 10^{-16}, which approximates that of the hydroxide. The concentrations of the solute in solutions A and B are large enough to permit precipitation of such a double salt. In solutions C, D, E, F, however, concentrations are too dilute for such precipitation to occur. Apparently in these solutions adsorption rather than hydrolysis accounted for the loss in strength. This is substantiated by reference to the type of container: solutions of identical content showed greater losses in the polyethylene than in Pyrex containers.

The solubility products calculated for the hydrolytic uranium compound agreed fairly closely with the published value. Moreover,

Table 3.--Recalculated solubility products of solutions which exhibited unusually large changes in pH.

Solution	Original concentration in γ/ml	Percent of original concentration remaining	pH		Solubility product using final pH	Solubility product using initial pH
			Initial	Final		
Uranium H (in Pyrex)	0.1	82	6.7	3.8	1.38×10^{-27}	8.7×10^{-22}
Uranium I (in polyethylene)	0.1	52	6.5	6.1	3.48×10^{-23}	
Lead D (in Pyrex)	0.1	39	6.4	6.3	7.54×10^{-23}	
Lead E (in polyethylene)	0.1	34	6.4	3.8	6.54×10^{-28}	1.04×10^{-23}
Thorium G (in Pyrex)	1	22	6.4	6.1	2.39×10^{-39}	
Thorium H (in polyethylene)	1	25	6.4	3.5	1.08×10^{-48}	4.3×10^{-37}

solutions A, B, C, and D clearly showed the yellow hydrolytic precipitate adhering to the walls of the container (notably the plastic), or deposited on the bottom. However, solutions of identical content again showed greater loss in polyethylene than in Pyrex. This would indicate that, in addition to hydrolysis, some adsorption had taken place.

Thorium solutions A, B, D, E, H, I, and J seem to indicate that adsorption had taken place, whereas solutions C, F, G, K, and L suggest that hydrolysis had also been possible. Because of the relatively great uncertainty present in the calculations, it is difficult to draw any valid conclusions concerning how the thorium solutions lost strength.

Solutions of Pb^{++} and UO_2^{++} which were too acid for hydrolysis to occur also showed no losses from adsorption. So, if the pH of these solutions is adjusted to prevent loss by hydrolysis and precipitation, the solution is also protected against loss by adsorption. However, thorium solutions which were as dilute as 0.1γ Th^{4+}/ml seem to lose strength even when the solution is too acid for hydrolysis. The higher valence of thorium increases the tendency for the ion to be adsorbed.

Regardless of whether adsorption, or hydrolysis, or both caused the loss of concentration of solution, it was impossible to restore the original strength by vigorously shaking the solution for one minute. Even that material which had been removed as hydrolytic precipitate was bound in some manner, such as adsorption, to the walls of the container and could not be redispersed throughout the solution even by shaking.

Adsorption on the walls of the container cannot be eliminated by the substitution of polyethylene containers for glass bottles; in fact losses are greater when plastic containers are used.

On glass the adsorption can take place through the action of base exchange, chemisorption, and Van der Waal's adsorption. On polyethylene plastic there are no unsatisfied valence-type attractive forces, and only the Van der Waal's adsorption is operative. The results indicate that if adsorption by chemisorption and base exchange is present to any extent, it is far less effective than adsorption through Van der Waal's forces, because for solutions of the same concentration and acidity adsorption was generally greater in plastic than in glass. Such a physical type of adsorption varies directly with the degree of roughness of the adsorbing surface, that is, pits and humps that increase the specific surface available for adsorption, as well as scratches or imperfections, and the exposed edges of the solid phase, where the attractive forces are the strongest. The characteristics of glass in these respects should be much less conducive to adsorption than the softer plastic.

The solutions with which this research was concerned were composed only of the one salt in aqueous solvent. However, in samples of natural waters, other anions and cations would also be in solution. The metal ions could react with the various anions in these waters and be precipitated, or other molecules could act as carrier for the metal solute and help remove it from solution. On the other hand, there would be (1) existence of inter-ionic attractive effects, and (2) the possibility of the metal ion's forming stable complexes with the other ions, both of which would have the effect of increasing the solubility of the metal solute.

Only additional experiments can reveal the net effect of these factors on the stability of the solutions.

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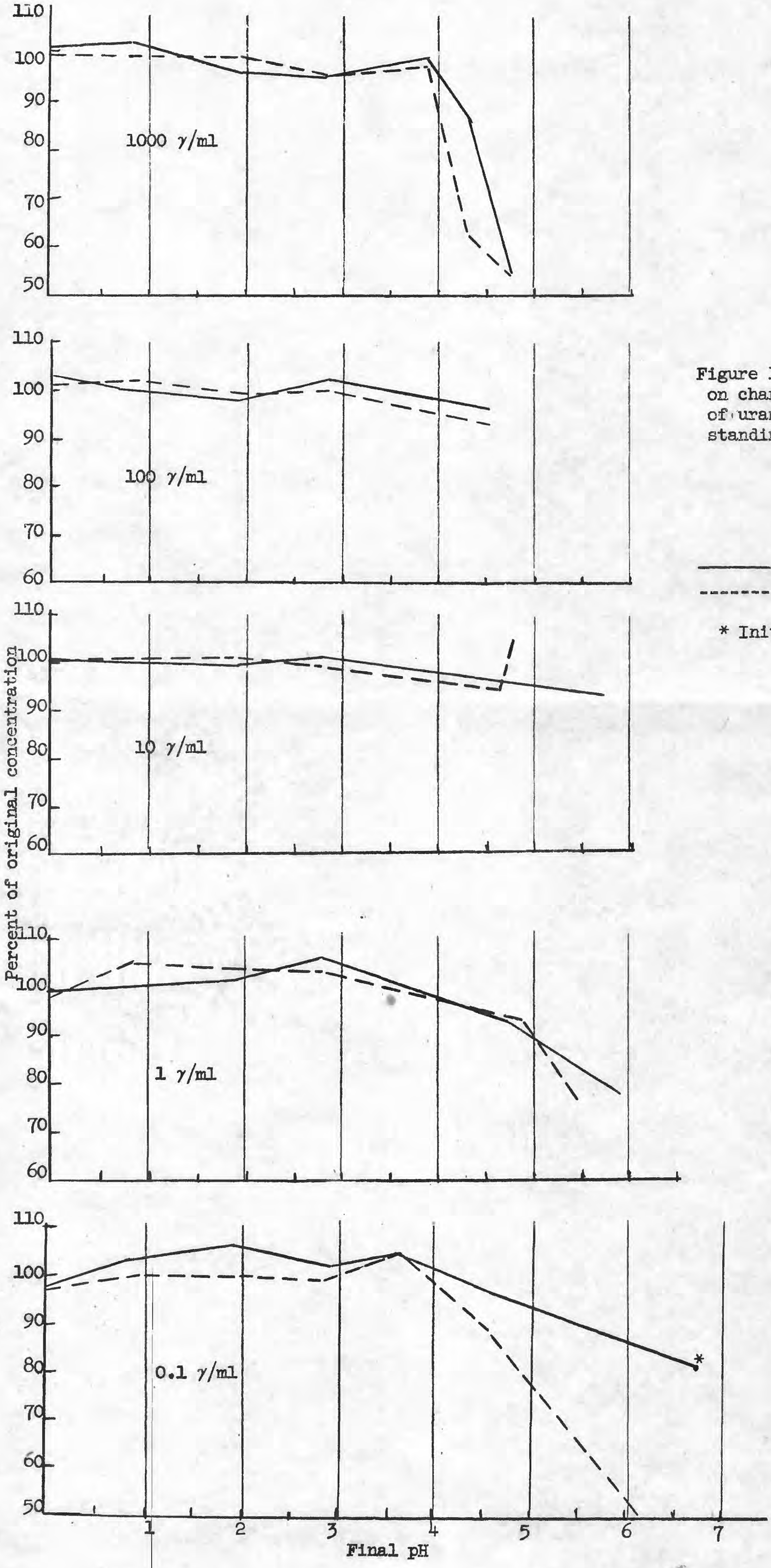

Figure 1.--Summary of data on changes in concentration of uranium solutions after standing for 2 1/2 months.

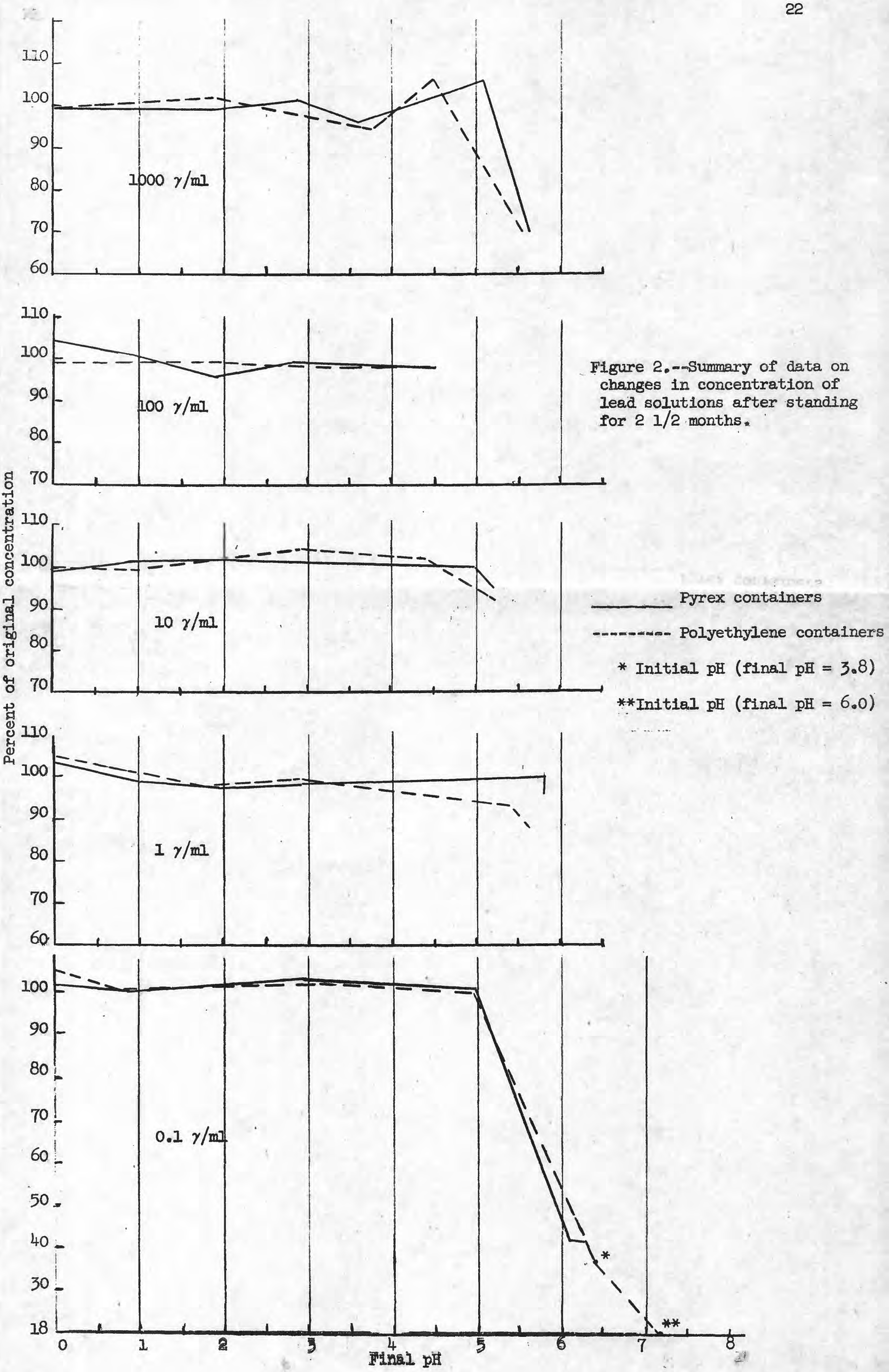

Figure 2.--Summary of data on changes in concentration of lead solutions after standing for 2 1/2 months.

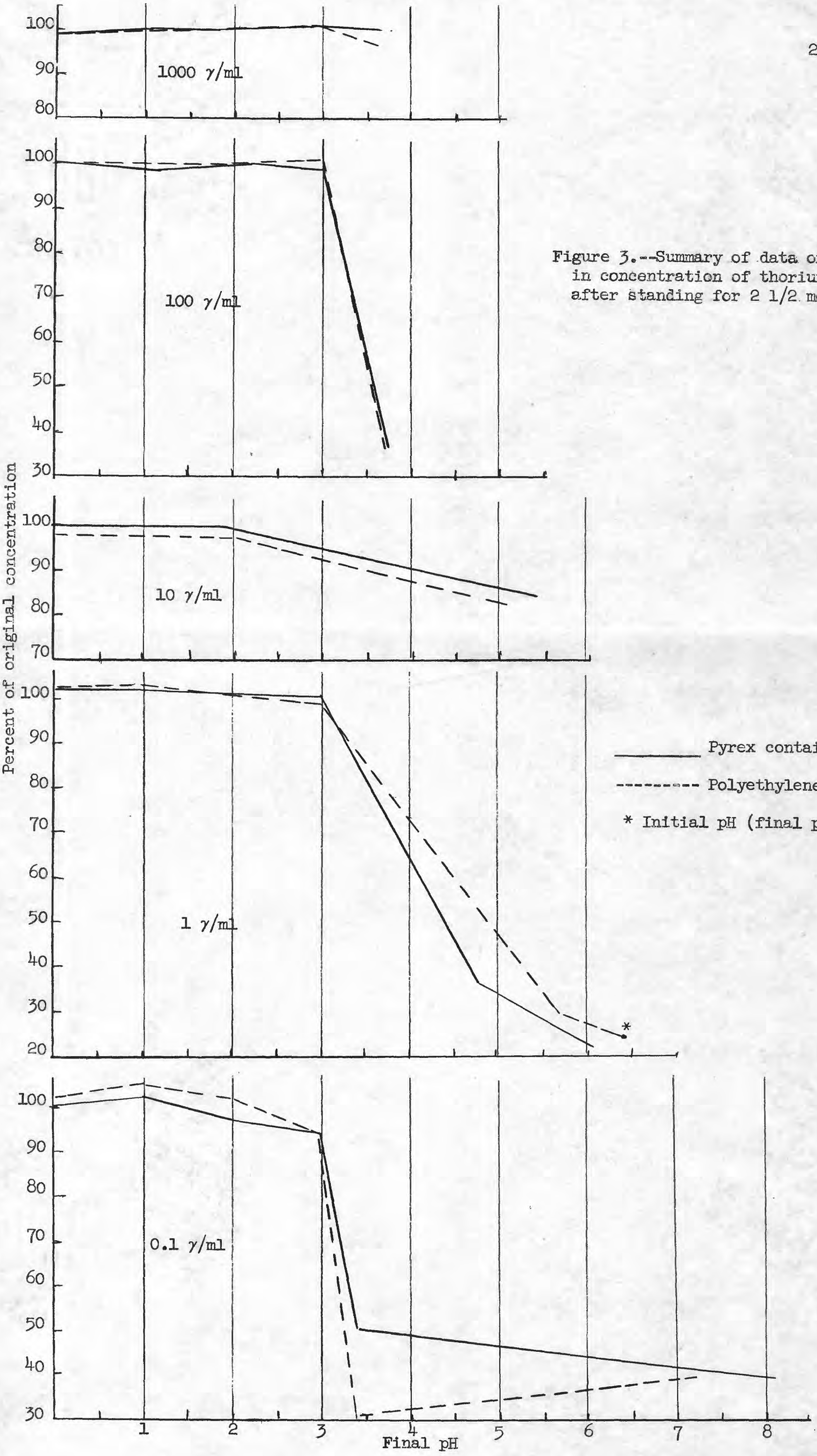

Figure 3.--Summary of data on changes in concentration of thorium solutions after standing for 2 1/2 months.