

# Complexes of Ferrous Iron With Tannic Acid

by J. D. HEM

CHEMISTRY OF IRON IN NATURAL WATER

---

GEOLOGICAL SURVEY WATER-SUPPLY PAPER 1459-D



**UNITED STATES DEPARTMENT OF THE INTERIOR**

**FRED A. SEATON, *Secretary***

**GEOLOGICAL SURVEY**

**Thomas B. Nolan, *Director***

## CONTENTS

---

	Page
Abstract.....	75
Acknowledgments.....	75
Organic complexing agents.....	75
Tannic acid.....	77
Properties.....	78
Dissociation.....	78
Reducing action.....	79
Laboratory studies.....	79
Analytical procedures.....	80
Chemical reactions in test solutions.....	81
No tannic acid.....	84
Five parts per million of tannic acid.....	84
Fifty parts per million of tannic acid.....	85
Five hundred parts per million of tannic acid.....	86
Rate of oxidation and precipitation of iron.....	87
Stability constants for tannic acid complexes.....	88
Comparison of determined and estimated Eh.....	91
Action of tannic acid or related compounds in natural water.....	93
Literature cited.....	94

---

## ILLUSTRATIONS

---

	Page
FIGURE 9. Effect of tannic acid on stability of dissolved iron at pH 4.0..	88
10. Effect of tannic acid on stability of dissolved iron at pH 6.0..	89

---

## TABLES

---

	Page
TABLE 1. Effect of 0.5 and 50 ppm of tannic acid on aged solutions containing ferrous and ferric iron.....	82
2. Effect of 500 ppm of tannic acid on aged solutions containing ferrous and ferric iron.....	82
3. Measured and computed values of Eh.....	93



# CHEMISTRY OF IRON IN NATURAL WATER

---

## COMPLEXES OF FERROUS IRON WITH TANNIC ACID

---

By JOHN D. HEM

---

### ABSTRACT

Solutions of tannic (digallic) acid at concentrations of 5 or 50 parts per million reduce dissolved ferric iron to the ferrous state when the pH is less than 4. In solutions with a pH of 4 or more, a black material containing ferric iron and tannic acid is precipitated. In a solution containing 500 parts per million of tannic acid, a ferrous complex forms at a pH of more than 5. This complex is oxidized at a slow rate, and some ferrous iron remains in solution after a month of storage in contact with air. Uncomplexed ferrous iron is oxidized and precipitated from solution in a few hours or less at pH levels of more than 5.

The approximate value of the first dissociation constant for tannic acid is between  $1 \times 10^{-5}$  and  $1 \times 10^{-6}$ . The stability constant for the ferrous complex is comparable in magnitude to that of the pink bipyridine complex used in the determination of iron.

### ACKNOWLEDGMENTS

The work described here was done as part of the research on the chemistry of iron in natural water by the U.S. Geological Survey. The author was assisted in the laboratory work by E. C. Mallory. The manuscript was reviewed by Dr. H. S. Puleston and Dr. G. H. Splittgerber of the Department of Chemistry, Colorado State University, Fort Collins, Colo.

### ORGANIC COMPLEXING AGENTS

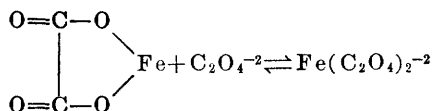
Iron combines readily with many other ions and forms "complexes," which generally have an ionic charge. The charge of most complexes is positive, but neutral and anionic complexes also exist. The literature contains much quantitative information, including stability constants, on complexes of iron with organic ligands. (A ligand is a negatively charged chemical unit that combines with a positively charged ion by coordinate bonding.) Some of these complexes have been used in the determination of iron by colorimetric procedures. The bipyridine method for iron, for example, depends on the formation of a highly stable and intensely colored ferrous complex. The avail-

able data on organic complexes are summarized by Bjerrum, Schwarzenbach, and Sillen (1957).

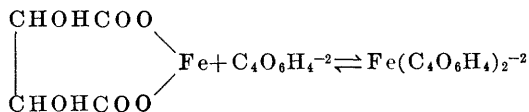
A special type of complexing between inorganic ions and organic structures is termed "chelation." In chemical terms, a chelate compound or ion is a ring structure which contains a central atom, usually of a metal, that is tied by both coordinate and polar valence bonds to an organic segment. The chelate ions or compounds generally display properties very different from the uncomplexed metallic ions, and this fact has led to the use of chelation in analytical chemistry (use of ethylenediaminetetraacetic acid in hardness titrations, for example). Some literature relating to the weathering of rocks and to the behavior of chemical elements in soils uses the term "chelation" rather loosely as a synonym for the formation of any complex of a metal and an organic ligand.

Delong and Schnitzer (1955) report that leaf extracts and solutions from forest canopies and forest floors are "capable of the mobilization and transportation of iron," and they believe that the active material in these extracts is an "acidic polysaccharide." Okura and Goto (1955) note that the oxidation of iron is retarded by "humic substances," a term commonly used to denote the organic material carried in leach from organic debris in soils, forests, and swamps. Obviously, this organic material is ill defined chemically and could hardly be characterized by a single specific structural formula. Systematic investigation of the chemical behavior of iron in the presence of organic extracts, however, requires some definite knowledge of the composition of the compounds involved.

Some organic complexes with iron have been studied in detail. Oxalic acid, which occurs in many varieties of vegetation, forms the anion  $\text{Fe}(\text{C}_2\text{O}_4)_2^{-2}$  as its most stable ferrous complex. The equilibrium constant for the reaction



is given as greater than  $7 \times 10^2$  by Schäfer and Abegg (1905). Tartaric acid forms a similar ferrous complex according to the reaction



which has a stability constant of  $7.1 \times 10^4$  (Toropova, 1945). Ferric complexes formed with oxalic and tartaric acid are stronger than the ferrous complexes.

Citric acid forms several complexes with ferrous iron that are less stable than the complexes formed with oxalic and tartaric acid, but the ferric citrate complex is as strong as the ferric complexes with oxalate and tartrate. Oxalic and tartaric acids have dissociation constants of more than  $10^{-5}$  (Schaap, Laitinen, and Bailar, 1954; Cannan and Kibrick, 1938), so both would be fully dissociated in most of the pH range of natural water.

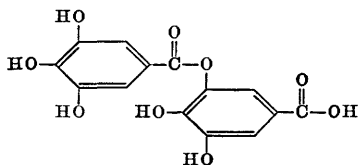
Among the other organic ions for which both ferric and ferrous stability constants have been determined are malonate,  $\alpha$ -amino- $\beta$ -mercaptopropionate, and several of the chelating agents related to ethylenediaminetetraacetic acid. All these ligands form strong ferric complexes.

One would expect complexed ferrous iron to be stable only in reducing environments. The complexing does not alter the general stability relationship expressed by the Eh-pH diagram in an earlier chapter of this study (Hem and Cropper, 1959), which was based on the ultimate equilibrium between ferrous and ferric ions. When complexing takes place, however, both Eh and pH may be altered, and the rate of oxidation or reduction may be considerably slower than when complexing is absent. Hence, equilibrium in the presence of complexing may be reached very slowly.

The published data on organoferrous or ferric complexes do not include anything on gallic acid or any closely related compounds; therefore, nothing directly applicable to the tannic acid complexes could be found.

### TANNIC ACID

Tannin is present in many types of plant material. According to Brewster (1948), natural tannin is mostly made up of the chemical compound gallocatechin. It has a complex molecule with the basic structure of 1 glucose molecule bonded to as many as 5 molecules of gallic acid. In water solution, the tannin molecule hydrolyzes to give glucose and digallic acid. The structural formula of digallic acid is



The tannic acid used in these experiments is represented by the above formula and has a molecular weight of 322. Tannic acid is obtained commercially from galls of oak, sumac, and willow and occurs in green algae, mosses, brown seaweed, ferns, pore fungi, and in about one-third of the families of flowering plants (Gibbs, 1950). The behavior

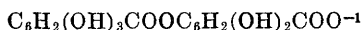
of ferrous and ferric iron in solutions containing tannic acid may be analogous to their behavior in natural water that contains organic extracts. Because tannic acid is available in pure form, the behavior of mixtures of this acid and ferrous and ferric iron is of considerable interest.

Shapiro (1958) states that coloring materials present in natural water are "ultraviolet fluorescing dicarboxylic hydroxy aliphatic organic acids of molecular weight approximately 450." He also states that these materials are probably unsaturated and contain no nitrogen and that they are "capable of keeping iron in a nonprecipitable state at a pH as high as 9.5 for at least several weeks." Although tannic acid is an aromatic rather than an aliphatic compound and also differs in other ways from the material studied by Shapiro, tannic acid may also retain iron in solution under some conditions.

#### PROPERTIES

The carboxyl hydrogen in the digallic acid molecule is the source of the acidic properties of tannic acid. The substance is in effect a monoprotic acid, inasmuch as the OH groups attached to the benzene rings do not readily yield protons.

The anion that results from the dissociation of tannic acid is



which can be abbreviated for present purposes to the symbol  $T^{-1}$ . This anion can combine with ferrous iron to form complexes of the type  $T\text{Fe}^{+1}$  or  $T_2\text{Fe}$ . Tannic acid complexes with ferric iron may consist of large highly colored molecules that behave as colloids. The well-known black material produced by mixing tannic acid and ferric iron solutions is a ferric complex.

#### DISSOCIATION

A solution containing 50 mg (milligrams) of tannic acid was titrated with 0.0167*N* sodium hydroxide. The pH of the solution being titrated was continuously observed with a pH meter. The resulting titration curve indicated that the carboxyl hydrogen of the acid was fully titrated at pH 7.5. The dissociation constant for tannic acid estimated from these titration data is between  $10^{-6}$  and  $10^{-5}$ . The published value for the first dissociation constant of gallic acid is  $4 \times 10^{-5}$  (Lange, 1956, p. 1199); therefore, a value between  $10^{-6}$  and  $10^{-5}$  probably is logical for digallic (tannic) acid.

The phenolic hydrogens of the tannic acid molecule become dislodged at higher pH values. The titration experiment indicated that these hydrogens are available at pH 9 and probably to some extent at pH 8. The titration curve, however, did not show any individual deflections but rose most steeply in the vicinity of pH 10.



The increasing intensity of the color of the solution suggested that side reactions probably were occurring to decompose the tannic acid.

From the apparent dissociation constant, tannic acid is found to be, in effect, undissociated below pH 4 and less than half dissociated even at pH 5. Consequently, complexing should not happen when ferrous or ferric ions combine with digallate ions in a strong acid solution ( $\text{pH} < 4$ ). Chelation of ferrous or ferric iron by tannic acid probably would require the dislodgment of some of the phenolic hydrogen of the molecule to provide a type of bonding that could tie up a single cation at two points in the molecule. The titration results as well as the values given in the literature for dissociation of phenol ( $K \approx 10^{-10}$ ) indicate that the phenolic hydrogens are not extensively affected until the pH reaches 9 or more. Therefore, in the pH range of natural water (generally below 9), chelating action (in the strict interpretation of the term) of tannic acid toward iron is likely to be rather weak.

#### REDUCING ACTION

Gallic acid is a reducing agent (Brewster, 1948, p. 660), and reduction is important in the reactions that may occur between tannic acid and dissolved ferrous and ferric iron. The reducing action was approximately evaluated by potentiometric titrations in which potassium permanganate was used. The titration gave well-defined end points whose position ranged from  $E_h \approx 0.85$  v (volt) when the starting pH was 2.0 to  $E_h \approx 0.55$  v when the starting pH was 9.0. Although the response of the redox system to additions of permanganate was sluggish, about six times as much permanganate was consumed at pH 2 as at pH 9. The reducing capacity of tannic acid is thus shown to be greater in acid than in alkaline solutions. The fact that permanganate is a more effective oxidant in acid than in basic solution may be responsible for some of the difference. The color of the solution deepened during the titration and resembled strong tea at the end point, but no precipitation took place.

The reducing action of tannic acid is assignable, in part at least, to the phenolic hydrogens in the molecule. The role of these hydrogens obviously changes with the pH. As the pH rises, their increasing availability as acidic hydrogen would probably decrease their effectiveness in reducing reactions.

In the process of reduction, the tannic acid itself is oxidized. The oxidation can proceed in aerated water at neutral pH; hence, such solutions are not stable, although the oxidation is slow.

#### LABORATORY STUDIES

In order to study some of the reactions among ferrous and ferric iron and tannic acid, a series of solutions was prepared. A stock

solution was made up of about 10 ppm (parts per million) of iron in hydrochloric acid at a pH of about 1.2. The water used contained oxygen dissolved from the air. An aliquot of the stock solution was adjusted to pH 2 by adding solid sodium carbonate. The aliquot was then divided into 7 portions, each of which was placed in a tightly stoppered plastic bottle. Similar aliquots of the stock solution were adjusted to pH levels of 3.0, 4.0, 5.0, and 6.0, and 7 bottles of each aliquot were set aside.

From time to time over a period of 30 days, 1 of the 7 bottles of each aliquot was opened, and the Eh of the sample was determined. The sample was then passed through a plastic filter membrane with openings 0.45 micron in diameter to remove precipitated or colloidal ferric iron. The concentrations of the ferrous and the total iron in the filtrate were then determined by the bipyridine procedure. The concentration of the ferric iron is the difference between the total iron and the ferrous iron concentration.

The entire series of determinations was repeated with stock solutions containing the same amount of iron, plus 5 or 50 ppm of tannic acid. The acid was added before the pH was adjusted.

In order to observe the effects of more concentrated tannic acid solutions, another series of samples was prepared by using a slightly different technique. Two stock solutions were prepared; one contained 0.1 mg of ferrous iron per milliliter and the other 5 mg of tannic acid per milliliter. Equal parts of these solutions were mixed and diluted fivefold; concentrations of 10 ppm of iron and 500 ppm of tannic acid resulted. The pH of the aliquots of diluted solution was adjusted to a predetermined value by using solid sodium carbonate, and each aliquot was divided into 6 portions for analyzing after storage intervals of as much as 30 days. The pH of these aliquots ranged in unit steps from 2.0 to 9.0. An airspace was left in the bottles in which the portions were stored, but the bottles were kept stoppered until the analysis was begun. The same analytical procedure was used except that some modifications were required in the iron determination because of interference by tannic acid.

#### ANALYTICAL PROCEDURES

The bipyridine procedure for determining the presence of iron in solution depends on the formation of a stable colored complex of ferrous iron with the organic reagent. According to the procedure used in routine water analysis, all iron present must be reduced to the ferrous state by addition of hydroxylamine. For this study, the ferrous iron was determined and, when possible, without adding the reducing agent. The total iron also was determined by the standard procedure.

When large amounts of tannic acid are present, the acid interferes in the iron determination if the standard procedure is followed. To avoid the interference in the samples that contained 500 ppm of tannic acid, the iron determination was modified. Hydroxylamine and hydrochloric acid were added to duplicate 2-ml aliquots to lower the pH and to break up complexes that might have formed. The hydroxylamine also reduced any ferric iron present to the ferrous state. The aliquots were then diluted to 29 mls. Bipyridine was added to one aliquot, and a pink color developed by dropwise addition of sodium acetate buffer. Care was taken to add only about one drop of the buffer in excess after maximum color development was reached. The pH in the final solution was between 3 and 3.5, which is within the range of stability for the bipyridine complex (Sandell, 1950, p. 378). However, in this range, the tannic acid-ferrous iron complex did not form. The aliquot that contained only the original sample, hydroxylamine, and hydrochloric acid was diluted with distilled water to the same volume as the aliquot in which the color had been developed, and was used as a blank in setting the spectrophotometer.

The hydroxylamine and hydrochloric acid did not bleach all the color from the solutions that had been held at pH 5 or more for several days. The remaining color was probably caused by oxidation products of tannic acid, but all the iron was probably brought into solution in the ferrous form by the hydroxylamine treatment.

In the solutions containing 5 ppm of tannic acid, interferences in the bipyridine procedure caused by the formation of tannic acid complexes were not noticeable. In the solutions containing 50 ppm of tannic acid, the effect of interference was noticeable at a pH of 4 or more. Because this effect was relatively minor, valid separate ferrous and ferric determinations could be made. For the 500-ppm tannic acid solutions, separate determinations were not possible, and only a total iron content is reported at a pH of more than 4. The tannic acid in this strong solution probably reduced all the dissolved iron to the ferrous form. Ferric iron was found in only 3 of the 48 determinations made on solutions containing 500 ppm of tannic acid.

#### CHEMICAL REACTIONS IN TEST SOLUTIONS

Results of the pH, Eh (redox potential), and iron determinations on the test solutions are given in tables 1 and 2. Measured values of Eh and computed values based on pH and iron content are given for selected test solutions in table 3.

TABLE 1.—Effect of 0, 5, and 50 ppm tannic acid

[Eh in volts, Fe concentration

No tannic

Initial pH	0 days				1 day				2 days			
	pH	Eh	Fe <sup>+2</sup>	Fe <sup>+3</sup>	pH	Eh	Fe <sup>+2</sup>	Fe <sup>+3</sup>	pH	Eh	Fe <sup>+2</sup>	Fe <sup>+3</sup>
2.0	2.0	0.761	1.9	8.0	2.1	0.758	2.7	7.2	2.0	0.746	2.2	7.5
3.0	3.0	.728	1.4	8.0	3.0	.728	1.8	6.0	3.0	.716	1.5	6.8
4.0	4.0	.473	.05	.02	4.0	.574	.15	.00	4.0	.556	.20	.00
5.0	5.1	.450	.00	.02	5.2	.521	.02	.00	5.3	.509	.00	.02
6.0	6.1	.420	.00	.08	6.2	.485	.00	.00	6.2	.479	.00	.00

5 ppm of

Initial pH	0 days				1 day				2 days			
	pH	Eh	Fe <sup>+2</sup>	Fe <sup>+3</sup>	pH	Eh	Fe <sup>+2</sup>	Fe <sup>+3</sup>	pH	Eh	Fe <sup>+2</sup>	Fe <sup>+3</sup>
2.0	2.0	0.716	5.9	4.2	1.9	0.710	7.0	3.0	1.9	0.705	7.8	1.8
3.0	3.0	.675	5.0	1.3	3.0	.666	6.2	.75	3.1	.651	6.8	.64
4.0	4.0	.538	2.6	.00	4.0	.521	3.4	.00	4.1	.461	3.6	.00
5.0	5.1	.455	.52	.00	5.1	.444	.75	.00	5.2	.420	.62	.02
6.0	6.1	.390	.11	.02	6.2	.414	.02	.02	6.3	.390	.00	.02

50 ppm of

Initial pH	0 days				1 day				5 days			
	pH	Eh	Fe <sup>+2</sup>	Fe <sup>+3</sup>	pH	Eh	Fe <sup>+2</sup>	Fe <sup>+3</sup>	pH	Eh	Fe <sup>+2</sup>	Fe <sup>+3</sup>
2.0	2.0	0.616	10	0.00	2.0	0.598	10	0.00	1.9	0.592	10	0.00
3.0	3.1	.550	7.8	.00	3.1	.533	8.0	.00	3.0	0.533	7.8	.00
4.0	4.2	.438	3.3	.05	4.2	.473	3.6	.00	4.2	.461	3.5	.00
5.0	5.0	.408	.32	.00	5.1	.420	.96	.00	5.1	.414	.50	.00
6.0	6.0	.372	.02	.08	6.1	.390	.02	.00	6.1	.390	.00	.08

TABLE 2.—Effect of 500 ppm of tannic acid on

[Eh in volts, Fe concentration

Initial pH	Observation 1					Observation 2					Observation 3				
	Time since start (days)	pH	Eh	Fe <sup>+2</sup>	Fe <sup>+3</sup>	Time since start (days)	pH	Eh	Fe <sup>+2</sup>	Fe <sup>+3</sup>	Time since start (days)	pH	Eh	Fe <sup>+2</sup>	Fe <sup>+3</sup>
2.0	0	2.0	0.66	9.4	0.0	3	2.1	0.64	10	0.0	7	2.1	0.65	10	0.0
3.0	0	3.0	.56	5.6	2.8	2	3.1	.52	3.2	7.6	6	3.1	.56	6.8	0.0
4.0	0	4.0	.50	5.0	5.0	2	4.0	.47			6	4.0	.52	8.5	0.0
5.0	0	5.2	.38		6.8	1	5.2	.44		7.2	5	5.8	.44		6.2
6.0	0	6.1	.39			2	6.5	.34		9.8	7	6.6	.43		9.8
7.0	0	7.0	.41		12.0	1	7.1	.34		9.2	6	7.1	.45		9.2
8.0	0	8.0	.33		10.0	5	7.6	.41		9.2	7	7.2	.40		9.8
9.0	0	9.0	.32		10.0	4	8.1	.40		9.8	6	7.7	.36		9.5

on aged solutions containing ferrous and ferric iron

in parts per million]

acid present

5 days				6 days				15 days				30 days			
pH	Eh	Fe <sup>+2</sup>	Fe <sup>+3</sup>	pH	Eh	Fe <sup>+2</sup>	Fe <sup>+3</sup>	pH	Eh	Fe <sup>+2</sup>	Fe <sup>+3</sup>	pH	Eh	Fe <sup>+2</sup>	Fe <sup>+3</sup>
2.0	0.768	2.2	7.8	2.0	0.740	1.6	7.5	1.5	0.799	2.6	7.5	1.4	0.812	3.3	6.5
3.0	.710	1.6	2.9	2.9	.710	1.9	2.6	2.4	.734	1.8	1.4	2.4	.722	2.2	.50
4.2	.455	.25	.02	4.1	.491	.20	.00	4.1	.426	.20	.02	4.5	.467	.28	.00
5.4	.435	.00	.00	5.4	.444	.00	.08	5.7	.408	.00	.00	6.8	.473	.00	.00
6.4	.414	.00	.00	6.3	.420	.00	.00	6.8	.390	.00	.00	8.2	.414	.00	.00

tannic acid

5 days				6 days				15 days				30 days			
pH	Eh	Fe <sup>+2</sup>	Fe <sup>+3</sup>	pH	Eh	Fe <sup>+2</sup>	Fe <sup>+3</sup>	pH	Eh	Fe <sup>+2</sup>	Fe <sup>+3</sup>	pH	Eh	Fe <sup>+2</sup>	Fe <sup>+3</sup>
1.8	0.705	8.8	1.4	1.7	0.693	9.0	1.2	1.9	0.681	9.5	0.30	1.3	0.705	10	0.00
3.0	.645	7.5	.30	3.0	.627	8.2	.00	3.1	.622	8.5	.00	2.6	.633	9.0	.00
4.3	.444	4.0	.00	4.5	.471	4.0	.00	4.9	.390	3.6	.00	4.6	.390	2.2	.00
5.4	.414	.32	.08	5.7	.432	.08	.02	5.9	.384	.00	.00	7.5	.372	.05	.00
6.5	.384	.00	.02	6.6	.414	.00	.02	7.5	.361	.00	.00	8.2	.365	.05	.00

tannic acid

6 days				9 days				15 days				30 days			
pH	Eh	Fe <sup>+2</sup>	Fe <sup>+3</sup>	pH	Eh	Fe <sup>+2</sup>	Fe <sup>+3</sup>	pH	Eh	Fe <sup>+2</sup>	Fe <sup>+3</sup>	pH	Eh	Fe <sup>+2</sup>	Fe <sup>+3</sup>
2.0	0.610	10	0.00	2.0	0.592	10	0.00	2.1	0.610	10	0.00	1.5	0.610	10	0.00
3.1	.538	7.8	.00	3.1	.533	8.2	.00	3.2	.550	7.8	.00	2.7	.544	7.8	.00
4.4	.461	2.7	.00	4.5	.467	2.5	.00	4.5	.432	2.0	.00	4.6	.461	2.5	.00
5.3	.420	.64	.08	5.5	.426	.20	.08	5.9	.402	.00	.00	6.5	.408	.00	.08
6.4	.396	.00	.00	6.4	.408	.00	.02	6.2	.390	.00	.00	7.5	.390	.00	.02

aged solutions containing ferrous and ferric iron

in parts per million]

Observation 4					Observation 5					Observation 6				
Time since start (days)	pH	Eh	Fe <sup>+2</sup>	Fe <sup>+3</sup>	Time since start (days)	pH	Eh	Fe <sup>+2</sup>	Fe <sup>+3</sup>	Time since start (days)	pH	Eh	Fe <sup>+2</sup>	Fe <sup>+3</sup>
11	2.1	0.64	10	0.0	19	2.2	0.63	10	0.0	32	2.2	0.64	10	0.0
10	3.1	.56	6.2	0.0	18	3.1	.53	4.5	0.0	31	3.0	.53	5.4	0.0
10	3.9	.53	6.2	0.0	18	3.9	.50	5.4	0.0	31	3.8	.53	5.0	0.0
12	5.8	.41	5.6		19	5.0	.49	5.0		23	5.0	.49	5.0	
14	6.6	.43	7.8		21	6.9	.37	6.8		28	6.7	.44	7.5	
13	7.1	.43	7.8		20	7.9	.41	7.1		29	7.7	.44	6.2	
12	7.5	.42	6.9		19	7.8	.37	6.2		28	8.4	.40	4.6	
11	7.6	.41	5.8		18	8.3	.36	5.5		27	7.9	.42	2.0	

## NO TANNIC ACID

Evidently, the stock solutions used for the first experiments originally contained mostly ferric iron. The solubility of ferric iron in oxidizing solutions at pH 3 is somewhat more than 10 ppm, but it is only a few hundredths of a part per million at pH 4 on the basis of computations of the behavior of ferric hydroxide similar to those used in other parts of this research work (Hem, in press). The solutions of pH 2 and 3 are supposedly relatively stable. At pH 2, the expectation of stability was approximately realized. However, at pH 3, a slow loss of ferric iron occurred; and after 30 days, less than a tenth of the original  $\text{Fe}^{+3}$  remained although the ferrous content had increased somewhat. The initial Eh was greater than the value that would be imparted by oxygen from the air, and the amounts of ferric and ferrous iron tend to become stable at an Eh below 0.70 v.

At pH values of 4, 5, and 6, all the ferric iron had been precipitated at the end of 30 days; in fact, most of it was precipitated as soon as the solutions had been adjusted to the desired pH level. At these pH levels, the precipitation of ferric hydroxide is a relatively rapid reaction.

## FIVE PARTS PER MILLION OF TANNIC ACID

A solution of 5 ppm of tannic acid (molecular weight 322) has a molality of  $1.5 \times 10^{-5}$ . At pH 2, in the presence of 5 ppm of tannic acid, all the iron in the solution is converted to the ferrous form in 30 days. At pH 3, the reaction is slower, but it seems nearly completed after 30 days. Most of the effectiveness of tannic acid as a reductant is the result of the pyrogallol rings within the molecule. The OH groups on these rings are electron donors. The composition of the oxidized product is somewhat indefinite, and the initial content of  $\text{Fe}^{+3}$  may have been more than the 4.2 ppm shown in table 1. If 4.2 ppm of  $\text{Fe}^{+3}$  was reduced, the implication is that each molecule of the acid can reduce at least 5 ferric ions to the ferrous form. Mechanisms of oxidation of phenolic substances are discussed by Brewster (1948, p. 596), who states that the ring may break in the process or coalesce with other ring structures.

At pH values greater than 3, the effectiveness of the reducing action is decreased. The observations made earlier in this discussion on the decreasing reducing power of tannic acid as the pH increases are substantiated by the behavior of the iron in these solutions.

Complexing does not seem to be a significant factor in the solutions containing only 5 ppm of tannic acid. The amount of tannic acid available in terms of molar concentration is only a tenth of the amount of iron; hence, only part of the iron would be complexed under the most favorable conditions. The ferric complex with tannic acid is a black material that can be filtered out of solution. Precipitates did

form in the more alkaline samples on standing, but they were not highly colored.

In general, low concentrations of tannic acid reduce ferric iron to ferrous iron, but the action is relatively weak when the pH is much greater than 3.0.

#### FIFTY PARTS PER MILLION OF TANNIC ACID

A solution of 50 ppm of tannic acid has a molality of  $1.5 \times 10^{-4}$ , which is approximately the same molality as that of the initial iron solution.

The 50-ppm tannic acid solution reduced the ferric iron faster than the 5-ppm solution did. At pH 2, all the iron was reduced by the time the first determination was made. With few exceptions, the solutions contained no dissolved ferric iron after standing for 1 day. However, some ferric iron was removed as a black ferric complex by tannic acid. The Eh measured in these solutions at pH 2, 3, and 4 was substantially less than the corresponding Eh when less tannic acid was present. At pH 5 and 6, however, the Eh in the 50-ppm tannic acid solutions was not much different from the Eh in the 5-ppm solutions. At the end of 30 days, the amount of ferrous iron retained in the 50-ppm solution was not significantly different from the amount retained in the 5-ppm solution.

The ferric-tannic acid complex was observed in all portions of the 50-ppm tannic acid solution except those at pH 2.0, which remained colorless. The black "ferric tannate" was filtered out before the iron determination was made. The absence of ferric iron in most of the samples containing 50 ppm of tannic acid probably resulted from precipitation of ferric tannates. The small amounts of ferric iron found in a few samples at pH 5 and 6 may represent a fraction of the precipitate that passed through the filter.

Evidence of the presence of ferrous complexes in these solutions is inconclusive. Much iron and tannic acid was lost at once from these solutions by the precipitation of the black ferric-tannic acid complex. Interference with the formation of the bipyridine complex in the iron determination occurs to a slight extent in the presence of 50 ppm of tannic acid. The concentration of bipyridine present during the determination is about 100 ppm and of tannic acid about 20 ppm. Tannic acid, however, is a larger molecule; therefore, the moles of bipyridine outnumber the moles of tannic acid by a factor of about 10. The determination is made at a pH where part of the tannic acid is undissociated and unavailable for complexing. Important interference by the tannic acid complex implies that this complex is considerably stronger than the bipyridine complex.

## FIVE HUNDRED PARTS PER MILLION OF TANNIC ACID

A 500-ppm solution of tannic acid has a molality of  $1.5 \times 10^{-3}$ , which represents a large excess of tannic acid as compared to iron. The behavior of this solution differed markedly from that of the weaker solutions of tannic acid. Part of the difference in behavior stems from the absence of ferric iron in the original stock solution. In the beginning of the experiment, therefore, no ferric iron was present to form ferric tannate or ferric hydroxide. The portions of the strong tannic acid solution, however, definitely indicated the formation of ferrous complexes.

When the pH adjustment was made, the iron evidently was complexed at once, and a colored clear solution resulted. The color of the solution varied according to the pH as follows: pH 2, a barely noticeable greenish yellow; 3, pale blue black; 4, blue black with slight purple cast; 5, deep purple. At pH values greater than 5, the solution was a deep wine red, becoming dark red brown as the pH approached 9.

The pH and Eh of each aliquot were determined after various periods of storage; the remainder of each aliquot was filtered through a plastic filter membrane and then the amount of iron in the filtrate was determined.

The black or blue-black material formed in solutions that contain ferric iron and tannic acid is a result of the lake-forming action of tannic acid molecules. This action is a type of colloidal association of the tannic acid and ferric hydroxide molecules and is not strictly a chemical reaction. In the pH range from about 4 to 5, the black material formed when the ferrous iron was oxidized fairly rapidly to ferric hydroxide and the tannic acid was mostly undissociated. At pH values more than 5, the tannic acid was more extensively dissociated, and ferrous complexes formed with these anions.

The ferrous complexes apparently are oxidized on standing and are slowly lost from solution. As the complexes with ferrous iron oxidize, ferric ions are released and black ferric tannate is precipitated. This precipitate was subsequently removed by filtration. Except at pH 2, where no complexing occurred, the greatest amounts of iron after 30 days were in solutions whose pH had been adjusted to 6.0 and 7.0. All the more acid and the more alkaline samples lost iron more rapidly, but they still contained 2 to 5.4 ppm of iron after a month, in contrast to the weaker tannic acid solutions in which practically no iron was retained after a month of standing at pH values more than 5. The rate of loss of iron indicates that the solutions of pH 6 and 7 might retain half of their original iron for at least 60 days.



The decreased stability of solutions at pH 8 and 9 probably relates to the decreased stability and reducing capacity of the tannic acid when raised to these pH levels. The decomposition of the tannic acid also is indicated by the fact that lowering the pH of the aged alkaline solutions in determining the iron did not remove all the color from the solution.

If the dissociation constant ( $K$ ) for tannic acid is assumed to be about  $10^{-6}$ , the amount dissociated at pH 5 will be barely equivalent to the iron concentration, but the amount dissociated at pH 6 will substantially exceed the iron content. The behavior of the solutions at pH 5 and 6 suggests that  $K$  for tannic acid is about  $10^{-6}$ , which approximately checks with the  $K$  obtained by titration.

#### RATE OF OXIDATION AND PRECIPITATION OF IRON

The rate at which iron is oxidized and lost from solution is a function of the pH and the tannic acid content. In the solutions in which tannic acid was not present in sufficient amount to complex ferrous iron, the oxidation rate was slowed only slightly. However, some effect was observed because of the reducing power of the tannic acid. When complete complexing occurred, and a large excess of tannic acid was present, the rate of the oxidation of iron seemed to be a function of the rate of oxidation of tannic acid.

Figures 9 and 10 summarize the behavior of the solutions containing from 0 to 500 ppm of tannic acid at initial pH values of 4.0 and 6.0. The curves on these diagrams were fitted to points plotted from data in tables 1 and 2 and represent general trends rather than exact rates of decrease of iron concentration.

At pH 4, a small amount of ferrous iron can be retained at an Eh in the range of 0.4 to 0.5 v. In figure 9, the amount of iron in the solution containing no tannic acid seems to be fairly stable after 4 days. In the presence of tannic acid, a considerably greater amount of iron remained in solution even after 30 days, but the amount was slowly decreasing.

At pH 6.0 (fig. 10), the solution containing no tannic acid lost iron rapidly and retained no detectable amount at the end of 1 day. Solutions containing small amounts of tannic acid also lost nearly all their iron in the first day, but they still retained detectable amounts of iron at the end of 30 days. Small differences of iron content in the samples containing 5 or 50 ppm of tannic acid after the first few days may not have any real significance. The upward trend of iron content in the 5-ppm tannic acid solution after 20 days, therefore, may not represent any actual tendency for precipitated iron to return to solution. The rate of loss of iron in the 500-ppm solution was

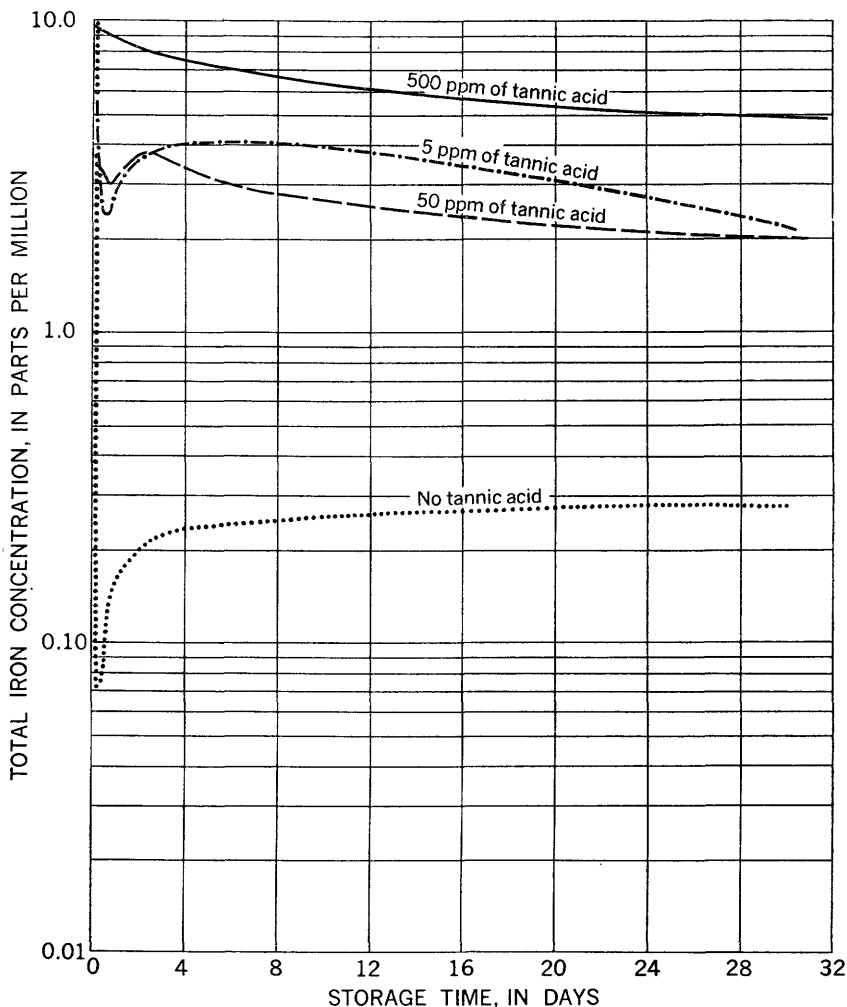


FIGURE 9.—Effect of tannic acid on stability of dissolved iron at pH 4.0. Initial iron content, 10 ppm.

very much less than that in the other solutions during the early part of the experiment.

#### STABILITY CONSTANTS FOR TANNIC ACID COMPLEXES

The composition of the ferrous complexes was not ascertained exactly in this work; therefore, the stability constants cannot be determined exactly. However, some approximations can be made from the observations that have been described.

The interference of the ferrous complexes in the bipyridine iron determination forms one basis for estimating the stability constant for the simplest cationic tannic acid complex. If the tannate ion (p.

78) is represented as  $T^{-1}$ , this complex would have the form  $TFe^{+1}$ . Tannic acid does not interfere at pH 3 because it is undissociated at this pH. The second dissociation constant for 2-2'bipyridine is  $4.3 \times 10^{-5}$  (Krumholz, 1949). In the presence of tannic acid and 2-2'bipyridine, the latter would become fully dissociated at a pH about 1.5 units smaller than that required for tannic acid if  $K$  is taken as  $10^{-6}$ . The behavior of the bipyridine complex, which forms at about pH 3, and of the tannic acid complex, which does not interfere below about pH 4, again indicates that a dissociation constant of about  $10^{-6}$  correctly predicts the behavior of tannic acid.

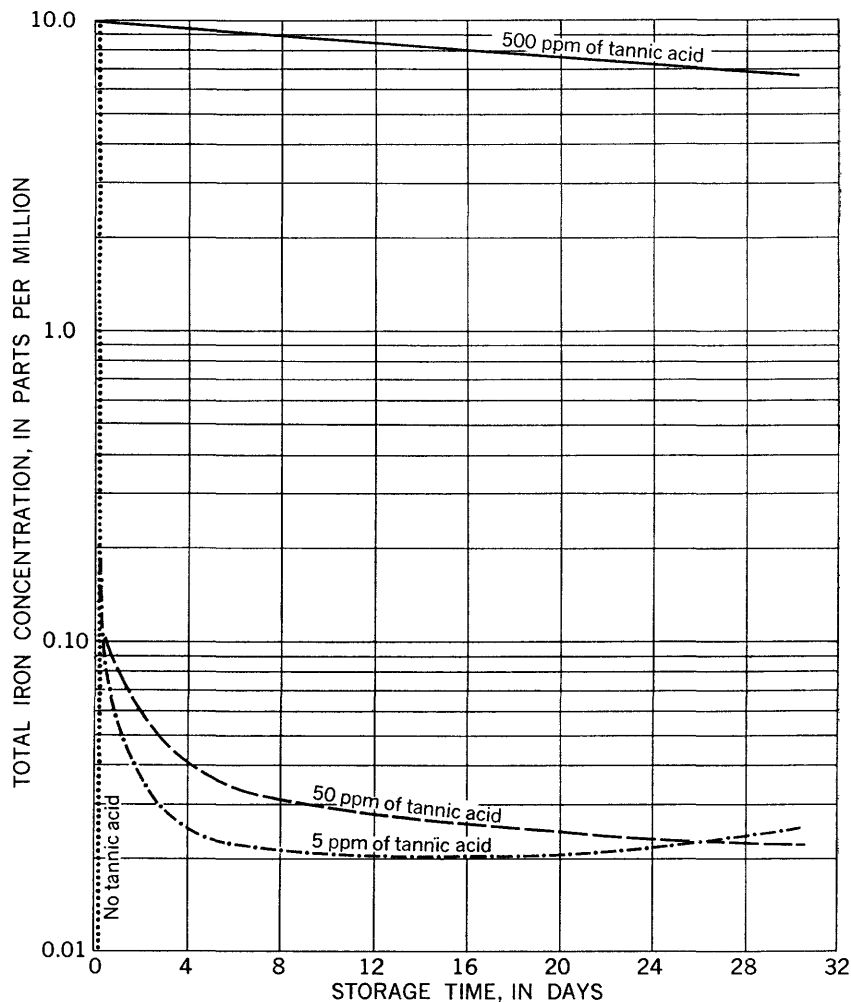


FIGURE 10.—Effect of tannic acid on stability of dissolved iron at pH 6.0. Initial iron content, 10 pp m\*

If a solution containing equivalent amounts of tannic acid and 2-2'-bipyridine is mixed with ferrous iron, the complex that will predominate can be predicted from their stability constants. The constant  $K_T$  for the tannic complex would be

$$K_T = \frac{[TFe^{+1}]}{[T^{-1}][Fe^{+2}]} \quad (1)$$

and, in similar terms, the constant  $K_{Bp}$  for the bipyridine complex would be

$$K_{Bp} = \frac{[Bp_3Fe^{+2}]}{[Bp]^3[Fe^{+2}]} \quad (2)$$

(The red complex with<sup>5</sup> bipyridine is indicated by Krumholz (1949) to have three units of bipyridine to each ferrous ion). The value of  $K_{Bp}$  given by Krumholz is  $3.8 \times 10^{17}$ . No value for  $K_T$  is available in the literature, but an estimate of its magnitude is possible from the observations of the complex that predominated at different levels of pH and concentrations of the reagents.

When the iron determinations were made in solutions containing tannic acid, equilibria represented by equations 1 and 2 occurred in the same solution. The  $[Fe^{+2}]$  terms appearing in both equations must be identical at equilibrium; hence,

$$\frac{[TFe^{+1}]}{[T^{-1}]K_T} = \frac{[Bp_3Fe^{+2}]}{[Bp]^3K_{Bp}}$$

Solving for  $K_T$ ,

$$K_T = \frac{[TFe^{+1}][Bp]^3K_{Bp}}{[T^{-1}][Bp_3Fe^{+2}]}$$

Values for  $[T^{-1}]$  depend on the pH; thus, if a first dissociation constant of  $10^{-6}$  for tannic acid is assumed,

$$[T^{-1}] = \frac{10^{-6} \times [TH]}{[H^{+1}]}$$

and by substituting this value for  $[T^{-1}]$  in the  $K_T$  formula,

$$K_T = \frac{[TFe^{+1}][H^{+1}][Bp]^3K_{Bp}}{[TH][Bp_3Fe^{+2}] \times 10^{-6}}$$

Activity values can be estimated from concentrations of the reagents added, but the magnitude of activity-coefficient corrections is not fully known.

At pH 5, the strong tannic acid solution gave a tannic acid complex that obscured the bipyridine complex. The solution contained known total amounts of iron, tannic acid, and bipyridine. If the assumptions are made that 90 percent of the ferrous iron is complexed with

tannic acid and that the remainder appears as the bipyridine complex, then  $K_T$  can be estimated to be between  $10^{13}$  and  $10^{14}$ . The assumed molality values for activity terms are

$$\frac{[TFe^{+1}]}{[Bp_2Fe^{+2}]}=9$$

$$[Bp]=4 \times 10^{-4}$$

$$[H^{+1}]=10^{-5}$$

$$[TH]=10^{-4}$$

Essentially all the bipyridine added is in this form and more than 90 percent of the tannic acid present at this stage has this form. The above assumptions probably give a minimum value for  $K_T$ .

The  $K_T$  thus computed is obviously only approximate, but it does indicate that the strong ferrous iron-tannic acid complex will be a dominant feature in solutions containing ferrous iron and enough dissociated tannic acid to react with all the iron. The other evidence obtained in these studies, however, indicates that the ferrous complex is slowly oxidized in contact with air and that iron is thus lost from solution. The  $K_T$  does not reflect oxidation effects.

#### COMPARISON OF DETERMINED AND ESTIMATED EH

Eh values were computed for the solutions used in this study for comparison with the measured values. In the solutions in which both the ferric and ferrous iron were present, the computation of the Eh was based on the observed ratio of ferric to ferrous activity and the Nernst equation,

$$Eh = E^\circ + \frac{0.0592}{n} \log \frac{A_{Fe^{+3}}}{A_{Fe^{+2}}}$$

where  $E^\circ$  is the standard redox potential for the oxidation of the ferrous to the ferric species, and  $n$  is the number of electrons lost by the reduced species on oxidation. The activities of the ferric and ferrous forms are indicated by  $A$ . In many of the solutions, the ferric iron was below the limit of detection. In these instances, where the pH was 3.0 or less, a  $10^{-7}$ -molal or about 0.006-ppm activity of ferric iron was assumed. This concentration is about the lowest limit in which ferric iron can still be detected. (See table 3.) At a higher pH, the ferric iron value was taken from earlier computations that used the maximum iron activity as a function of pH (Hem, in press).

If both ferrous and ferric activities could not be detected, no computation of Eh could be made. The final Eh value for each set of observations in table 3 represents the oldest aliquot that still contained ferrous iron in measurable amounts. The period between initial and final observations was about 30 days.

TABLE 3.—*Measured and computed values of Eh*

pH at start of test	Eh (volts)			
	Start of test		End of test	
Measured	Measured	Computed	Measured	Computed
<b>No tannic acid</b>				
2.0	0.76	0.79	0.81	0.77
3.0	.73	.73	.72	.71
4.0	.47	.70	.47	.55
<b>5 ppm of tannic acid</b>				
2.0	0.72	0.74	0.70	<sup>1</sup> 0.56
3.0	.68	.68	.63	<sup>1</sup> .55
4.0	.54	.60	.39	.50
5.1	.46	.44	.37	.40
<b>50 ppm of tannic acid</b>				
2.0	0.62	<sup>1</sup> 0.56	0.61	<sup>1</sup> 0.56
3.1	.55	<sup>1</sup> .52	.54	<sup>1</sup> .54
4.2	.44	.52	.46	.49
5.0	.41	.47	.43	.40
6.0	.37	.37	.39	.35
<b>500 ppm of tannic acid</b>				
2.0	0.66	<sup>1</sup> 0.56	0.64	<sup>1</sup> 0.56
3.0	.56	.71	.53	<sup>1</sup> .55
4.0	.50	.61	.53	.55
5.2	.38	.40	.49	.41
6.5	.34	.15	.44	.10
7.0	.41	.03	.44	— .07
8.0	.33	— .14	.40	— .20
9.0	.32	— .30	.42	— .09

<sup>1</sup> Computed as maximum Eh for Fe<sup>+3</sup>=0.006 ppm (actual Fe<sup>+3</sup> below detection).

A difference of  $\pm 0.06$  v is probably within the limits of error of the Eh measurement. However, many of the computed values differ from the observed values by a wider margin than  $\pm 0.06$ . Most of the value differences in the first three groups of solutions do not follow a definite pattern and are probably associated with a lack of equilibrium or with deviations from assumptions about ferric concentrations. However, for the aliquots that contain 500 ppm of tannic acid and whose pH is greater than 5, computed values are much lower than measured values. The computed Eh values are based on the ratio of ferric to ferrous activities; by increasing the ratio the computed Eh is increased. The ratio can be increased either by increasing ferric activity or decreasing ferrous activity.

The ferric value itself is computed, but it cannot be increased much without invalidating the assumptions already made about the relation of ferric activity to pH. These assumptions have been reasonably supported by previous work (Hem and Cropper, 1959) and seem to agree with solutions that contained 50 ppm of tannic acid. A more logical procedure would be to lower the calculated activity of ferrous species because a part of the ferrous iron is utilized in tannic acid complexes. Thus, the comparison between a measured and a computed Eh could be used to estimate the proportion of ferrous iron that is complexed. At pH values of 8 and 9, the computed Eh is as much as 0.62 v lower than the measured value. If all the difference is ascribed to ferrous complexing, the ratio of complexed to uncomplexed iron may be as much as  $10^{10}$  to 1.

Although the Eh effect is a recognized method for determining the strength of complexes, the conditions in these experiments were not controlled carefully enough to justify any such computation here. The results in table 3 indicate a strong complexing effect and that in water where complexing occurs, the Eh cannot be simply estimated from the pH and the iron content.

#### **ACTION OF TANNIC ACID OR RELATED COMPOUNDS IN NATURAL WATER**

The ability of tannic acid to form complexes with ferrous iron and to retard the oxidation of ferrous iron in water is demonstrated by the work described in this report. The most marked effect, however, occurred in a relatively strong tannic acid solution of about  $10^{-3}$  molar. In the weak solutions, the effect on iron behavior is less noticeable. Some tendency for the reduction of ferric to ferrous iron was observed below pH 4, and possibly some reduction in the strong tannic acid solutions occurred at pH 5.

Concentrations of tannic acid that markedly affect oxidation of ferrous iron are probably higher than the concentrations usually found in surface or ground water. However, films of water surrounding soil particles may sometimes contain relatively high concentrations of tannic acid or similar organic compounds leached from vegetation and plant debris. The experiments performed suggest that these solutions might reduce solid-phase ferric iron if the pH is low enough, and might take iron into solution as a ferrous complex. The rate at which the complex would be destroyed when in contact with air is slow enough to permit the complexed iron to be transported, at least in part, either to the ground-water body or to a surface stream. In the ground-water reservoir, reducing conditions might prevent any subsequent oxidation of the iron. In the surface stream, the rate of oxidation of the complexed iron would be

slow enough to permit detection of iron in the organic part of the dissolved solids many miles downstream from the point where the iron was complexed and taken into solution.

The structure or composition of ferrous complexes with tannic acid has not been studied in this work. The thermodynamic constants derived are only approximations. However, the study does indicate some possible mechanisms for iron solution and transport in forested or other regions where organic debris might yield tannic acid or similar solutes to soil moisture, runoff, and ground-water recharge.

#### LITERATURE CITED

- Bjerrum, Jannik, Schwarzenbach, Gerold, and Sillen, L. G., (compilers), 1957, Organic ligands; pt. 1 of Stability constants of metal ion complexes: London, Chem. Soc. [London], Spec. Pub. No. 6, 105 p.
- Brewster, R. Q., 1948, Organic chemistry: New York, Prentice-Hall, 838 p.
- Cannan, R. K., and Kibrick, Andre, 1938, Complex formation between carboxylic acids and divalent metal cations: Am. Chem. Soc. Jour., v. 60, p. 2314.
- Delong, W. A., and Schnitzer, M., 1955, The mobilization and transport of iron in forested soils: Soil Sci. Soc. America Proc., v. 19, p. 360-368.
- Gibbs, R. D., 1950, Botany, an evolutionary approach: Philadelphia, Blakiston Co., 554 p.
- Hem, J. D., Restraints on dissolved ferrous iron imposed by bicarbonate, redox potential, and pH: U.S. Geol. Survey Water-Supply Paper 1459-B (in press).
- Hem, J. D., and Cropper, W. H., 1959, A survey of ferric-ferrous chemical equilibria and redox potentials: U.S. Geol. Survey Water-Supply Paper 1459-A.
- Krumholz, P., 1949, Ferrous mono  $\alpha,\alpha'$ -dipyridyl: Am. Chem. Soc. Jour., v. 71, p. 3654.
- Lange, N. A., 1956, Handbook of chemistry: Sandusky, Ohio, Handbook Publishers, Inc., 1969 p.
- Okura, Takeshi, and Goto, Katshumi, 1955, Oxidation of ferrous ion in natural water: Chem. Soc. Japan Jour., Indus. Chem. Sec., v. 58, p. 239-241.
- Sandell, E. B., 1950, Colorimetric determination of traces of metals: New York, Interscience Publishers, Inc., 673 p.
- Schaap, W. B., Laitinen, H. A., and Bailar, J. C., 1954, Polarography of iron oxalates, malonates, and succinates: Am. Chem. Soc. Jour., v. 76, p. 5868.
- Schäfer, Hans, and Abegg, R., 1905: Untersuchungen über die Elektroaffinität der Anionen I.; Zeitschr. Anorg. Chemie, v. 45, p. 293.
- Shapiro, Joseph, 1958, Yellow acid-cation complexes in lake water: Science, v. 127, p. 702.
- Toropova, V. F., 1945, Polarographic study of stability of the complexes of iron with tartaric acid: Jour. Gen. Chemistry, U.S.S.R., v. 15, p. 603.