

of data in the literature. Straight line variation of the logarithm of the dielectric constant with temperature was generally found in every case over the entire range the measurements had been carried out.

Equations for the change with temperature of the dielectric constant of the pure solvents and the solvent-water mixtures have been obtained through large scale graphical interpolation. As a rule, the calculated values agree very well with the observed ones. A short discussion has been given of the polarization of glycerol-water mixtures.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA,
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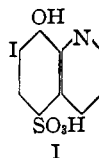
7-IODO-8-HYDROXYQUINOLINE-5-SULFONIC ACID AS A REAGENT FOR THE COLORIMETRIC DETERMINATION OF FERRIC IRON

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7-Iodo-8-hydroxyquinoline-5-sulfonic acid (I) dissolves in water to give a bright yellow solution which reacts with ferric ions, yielding blue to green colored solutions, the color and intensity varying with the iron concentration. The reaction is very sensitive and is best carried out in a solution acid to methyl orange paper. Ferrous ions give no color reaction and hence the reagent may be used to distinguish between ferrous and ferric iron. The color does not fade on standing, an advantage over the thiocyanate method.



Solutions

Standard Solutions of Various Ions.—Each standard solution was prepared from a good grade of salt, usually nitrate, chloride or sulfate, in the case of metallic ions, and from the potassium or sodium salt in the case of the non-metallic ions. Redistilled water was used (unless otherwise stated) and all solutions were kept in 30-ml. bottles that had been thoroughly cleaned and steamed out. Each bottle was fitted with a Pyrex glass dropper capped with a rubber stopper and nipple. Each dropper was calibrated, the capacities ranging from 18 to 28 drops per ml. The solutions were arranged according to the Periodic Chart and held in place on a wooden board, 45.5 cm. × 68.5 cm., in which were bored holes to carry the bottles. The concentration of the solutions was 400 mg. of the respective ion per liter, that is, 400 parts per million. Most of the solutions were aqueous, a few were in dilute acid (HCl, HNO₃ or H₂SO₄), and several were in concentrated acid.

In addition to the above solutions, more concentrated ones were prepared in the case of sodium, potassium, calcium and magnesium for use in preparing salt solutions for the determination of iron. These solutions contained 10 mg. of metallic ion per ml.

Standard Ferric Iron Solution.—A weighed quantity of pure ferrous ammonium sulfate, FeSO₄·(NH₄)₂SO₄·6H₂O, was dissolved in water, a few drops of concentrated sulfuric acid added and the iron oxidized by boiling with a little bromine. The excess bromine was expelled by boiling, the solution cooled to room temperature, transferred to

a volumetric flask, diluted to the mark and thoroughly mixed. Standard solutions containing 40 and 400 parts of Fe^{+++} per million, respectively, were prepared.

Reagent Solution.—Two-tenths gram of 7-iodo-8-hydroxy-quinoline-5-sulfonic acid dissolved in 100 ml. of water makes a satisfactory reagent solution.

The 7-iodo-8-hydroxyquinoline-5-sulfonic acid may be prepared according to Claus, German Patent 72,942, recorded in *Friedländer*, Vol. 3, page 964, and also in the *Jahresbericht der Chemischen Technologie*, 1894, page 625. Ten and twenty-five gram quantities of it may be purchased in a pure and crystalline form from G. D. Searle and Co., Chicago, Ill. The 7-iodo-8-hydroxyquinoline-5-sulfonic acid decomposes at 223° when heated in a capillary tube. Its aqueous solution is a bright yellow.

Procedure.—A preliminary procedure was carried out by placing a single drop of each of the standard solutions, respectively, in little glass cells (0.5 ml. capacity) used in P_{H} determinations according to the method of Brown.¹ These cells were lined up on a white glass plate which enabled rapid observation. No attention was paid to the acidity of the solution. Observations were repeated in the case of salts in acid solution. Measured quantities of these solutions were placed in small beakers, diluted with a few ml. of water and made weakly acid by partial neutralization with 6 *N* ammonium hydroxide. Each solution was transferred to a 50-ml. (210 mm. to mark) Nessler tube, 5 drops of iodohydroxyquinolinesulfonic acid solution added, the solution mixed, diluted to the 50-ml. mark with water, again mixed and then observed.

In observing the color reaction with ferric iron, a series of Nessler tubes was made up with varying concentration of the iron as follows. Measured quantities of standard ferric iron solution were transferred to Nessler tubes, 5 drops of iodohydroxyquinolinesulfonic acid solution added to each tube, the solutions mixed, diluted to the 50-ml. mark with water, again mixed and then observed. The observations are recorded in Table I.

TABLE I

Concn. of Fe^{+++} , parts per million	Remarks
"Blank," 5 drops reagent in 50 ml. water	Pale yellow
1 in 60	Not distinguishable from "blank"
1 in 30	Barely distinguishable from "blank"
1 in 15	Faint greenish tinge to the yellow solution
1 in 10	Faint greenish-yellow
1 in 7.5	Pale greenish-yellow
1 in 6	Pale greenish-yellow. Little more intense than the 1 in 7.5
1 in 3	Light yellowish-green. Much more intense than the 1 in 6
1 in 1.5	Bluish-green. Much more intense than the 1 in 3
8 in 1	Dark green. Four ml. of reagent used

Under the above conditions 1 part of ferric iron in 15 million parts of solution gives a faint greenish-yellow solution distinguishable from a "blank" containing only 5 drops of reagent and having a pale yellow color.

¹ Brown, *J. Lab. Clin. Med.*, 9, 239-244 (1924).

With 1 part of iron in 10 million parts of solution a greenish-yellow is obtained which is easily distinguished from the blank. One part of iron in 1.5 million parts of solution gives a bright bluish-green color. Higher concentrations give green colored solutions, the intensity increasing with the concentration of iron. The color is very stable to light and hence it is not necessary to prepare the set of standards and the sample solution at the same time, as is necessary in the case of the thiocyanate method. The same set of standards may be used all day. The reaction is affected by strong acids and bases, both of which destroy the color.

Observations with Various Ions.—None of the following ions give color reactions with 7-iodo-8-hydroxyquinoline-5-sulfonic acid: Lithium (Li^+), sodium (Na^+), potassium (K^+), rubidium (Rb^+), cesium (Cs^+), copper (Cu^{++}), silver (Ag^+), gold (Au^{+++}), calcium (Ca^{++}), strontium (Sr^{++}), barium (Ba^{++}), beryllium (Be^{++}), magnesium (Mg^{++}), zinc (Zn^{++}), cadmium (Cd^{++}), mercury (Hg^+ , Hg^{++}), boron (BO_3^{---}), aluminum (Al^{+++}), scandium (Sc^{+++}), yttrium (Y^{+++}), lanthanum (La^{+++}), cerium (Ce^{+++}), praseodymium (Pr^{+++}), neodymium (Nd^{+++}), samarium (Sm^{+++}), gadolinium (Gd^{+++}), dysprosium (Dy^{+++}), erbium (Er^{+++}), thulium (Tm^{+++}), ytterbium (Yb^{+++}), gallium (Ga^{+++}), indium (In^{+++}), thallium (Tl^{+++}), titanium (Ti^{++++}), zirconium (Zr^{++++}), hafnium (Hf^{++++}), thorium (Th^{++++}), germanium (Ge^{++++}), tin (Sn^{++} , Sn^{++++}), lead (Pb^{++}), vanadium (V^{++}), columbium (Cb^{++}), tantalum (Ta^{++++}), phosphorus (PO_4^{---}), arsenic (As^{+++}), antimony (Sb^{+++}), bismuth (Bi^{+++}), chromium (Cr^{+++}), molybdenum,² tungsten (W^{++++}), uranium (UO_2^{++}), sulfur (S^{--}), selenium,³ tellurium,⁴ manganese (Mn^{++}), rhenium,⁵ fluorine (F^-), chlorine (Cl^-), bromine (Br^-), iodine (I^-), iron (Fe^{++}), cobalt (Co^{++}), nickel (Ni^{++}), ruthenium (Ru^{+++}), rhodium,⁶ palladium (Pd^{++}), iridium (Ir^{++++}), platinum (Pt^{++++}).

Determination of Ferric Iron in Aqueous Solutions.—Measured quantities of solutions of various metallic salts (nitrates, chlorides or sulfates) were placed in 50-ml. Nessler tubes and to each tube was added a known amount of ferric iron. The solutions were diluted to approximately 5 ml.

² Metallic molybdenum was dissolved in *aqua regia* and the solution diluted with an equal volume of water.

³ Selenium was dissolved in concd. nitric acid and the solution diluted to 3 N HNO_3 .

⁴ Tellurium was treated with *aqua regia* and the mixture evaporated to dryness. Concentrated nitric acid was added to the residue and the mixture evaporated to dryness. This treatment was repeated several times and the residue finally taken up in 3 N HNO_3 .

⁵ Rhenium was treated with *aqua regia* and the mixture evaporated to dryness. Concentrated nitric acid was added to the residue and the mixture evaporated to dryness. This treatment was repeated and the residue finally taken up in water.

⁶ Rhodium was fused with potassium hydroxide and the fused mass dissolved in *aqua regia* and diluted 1:1 with water.

and made weakly acid⁷ with sulfuric acid. Then 5 drops of the 7-iodo-8-hydroxyquinoline-5-sulfonic acid reagent was added to each, the solutions were mixed by gentle shaking, diluted with water to the mark and thoroughly mixed. The colors were then compared with a set of standard solutions prepared in a similar way by adding 5 drops of the reagent to measured quantities of ferric iron in approximately 5 ml. volume made weakly acid with sulfuric acid, and finally diluted to the 50-ml. mark. The results are tabulated in Table II. It should be noted that the reagent solution is *yellow* but changes to *green* upon reacting with ferric ions, the color varying from a faint greenish-yellow to dark green, depending upon the iron concentration.

TABLE II
ANALYTICAL RESULTS

Soln.	Concentration of ions, parts per million											Fe ⁺⁺⁺ found, p. p. m.	
	Na ⁺	K ⁺	Ca ⁺⁺	Mg ⁺⁺	Co ⁺⁺	Ni ⁺⁺	Cu ⁺⁺	Al ⁺⁺⁺	Cr ⁺⁺⁺	Sn ⁺⁺⁺⁺	Ti ⁺⁺⁺⁺		Fe ⁺⁺⁺
1	200	200										0.1	0.1
2	200	200	200	200								.1	.1
3	200	200										.7	.7
4	200	200	200	200								.7	.7
5	200	200	200	200								2.2	2.2 ^a
6	200	200	200	200	3							0.7	0.7
7	200	200	200	200	8							.7	.6
8						3						.7	.5 ^b
9					1.7	1.7						.7	.7
10							0.4					.7	.6
11							0.7					.7	.4 ^c
12								4				.7	.7
13								8				.7	.6
14									0.3			.7	.7
15									1.5			.7	.6
16										1.7		.7	.7
17											1.7	.7	.7

^a One ml. of reagent was used in Solution 5 and in the standards. ^b Tints do not match. The addition of three more drops of reagent gave a very good color match corresponding to Fe⁺⁺⁺ 0.7 p. p. m. ^c Color bleached. Matching only approximate.

It will be noted that none of the colorless ions interfered with the color reaction nor did the colored ions interfere at the low concentrations used. Higher concentrations of the colored ions prevent accurate color matching. Cupric ions react with the reagent to give a white finely divided precipitate⁸ and hence would interfere with the color comparison if present in amounts greater than a few tenths of a part per million parts of solution. How-

⁷ Litmus paper was used at first and the acidity adjusted to a pale pink but in later experiments methyl orange paper has been employed and appears to permit a more uniform adjustment.

⁸ The copper appears to be precipitated completely by the reagent. We are investigating this reaction to see whether it can be used to determine copper quantitatively.

ever, the ferric iron may be detected *qualitatively* in the presence of much higher concentrations of copper. For example, a small excess of reagent was added to a solution containing Fe^{+++} 8 p. p. m. and Cu^{++} 40 p. p. m. A white precipitate was formed which settled upon standing for a few minutes, giving a dark green supernatant solution showing the presence of ferric iron. Salts that easily hydrolyze, such as those of tin or titanium, interfere with the color matching unless their concentration is very low.

We desire to express our thanks to G. D. Searle and Co., Chicago, Ill., who furnished us with the 7-iodo-8-hydroxyquinoline-5-sulfonic acid used in this investigation. J. D. Riedel-E. deHaën A. G., Hannover, Germany, supplied a number of pure salts of the rare elements, for which we are very grateful.

Summary

7-Iodo-8-hydroxyquinoline-5-sulfonic acid is a very sensitive colorimetric reagent for ferric iron, its yellow aqueous solution changing to blue or green upon the addition of ferric ions. It gives no color reaction with ferrous ions nor with a large number of other ions. The reagent is sensitive to 1 part of ferric iron in 10 million parts of solution when the observation is made in a 50-ml. (210 mm. to mark) Nessler tube. The reaction is best carried out in a solution acid to methyl orange paper. The color is stable to light (an advantage over the thiocyanate method) but is destroyed by strong acids and bases. Salts that hydrolyze easily or yield colored ions should not be present unless in very low concentration.

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[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORY OF BROWN UNIVERSITY]

PHOTOCHEMICAL STUDIES. XV. GERMANE. SOME REMARKS ON THE DECOMPOSITION OF AMMONIA SENSITIZED BY MERCURY VAPOR

BY HENDRIK ROMEYN, JR., AND W. ALBERT NOYES, JR.

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The photochemistry of germane has not been investigated previously. It should be of interest because of the similarity between this compound and methane. Taylor and Hill¹ found the latter compound, in contrast to other saturated hydrocarbons, not to undergo reaction under the influence of excited mercury atoms. Bates² found also that excited cadmium atoms transferred their energy to methane without producing reaction. Bates³ also investigated thoroughly the quenching of the resonance radiation of mercury by methane and found it to have an exceedingly

¹ Taylor and Hill, *THIS JOURNAL*, **51**, 2922 (1929).

² Bates, *Proc. Nat. Acad. Sci.*, **14**, 849 (1928).

³ Bates, *THIS JOURNAL*, **52**, 3825 (1930).