

JEWELRY

The chemist is, as a rule, not much interested in jewelry excepting from a scientific standpoint. He is vitally interested, however, in the fact that the demand for platinum in jewelry has rendered the price of this material so high that it is almost unobtainable. Unfortunately, the demand for platinum in this line is largely based upon its high price. Comparatively a small amount was used in jewelry until after the price of platinum exceeded that of gold. It then became a fad, amounting almost to a mania, to substitute platinum for gold, wherever one's means would permit of doing so. All efforts to produce a substitute for platinum, which would give results equal or superior to that metal in many respects, have proved almost futile, since the very evil which these attempts have sought to remedy is held up by the purveyors of platinum jewelry as a virtue; namely, its high price; and notwithstanding "a rose by any other name would smell as sweet," it must in the eyes of fashion also *cost as much, or more*; in fact, the more the better. Whether this condition is to continue indefinitely or be limited by a legal enactment is a question for our Government to decide. Fashion, like fortune, is fickle, and may change radically at almost any instant.

Stellite would in many cases substitute to great advantage for platinum in jewelry. It is almost the same color, possesses a higher luster, and retains its luster very much better than platinum, since it is so hard that it is not easily scratched or abraded by ordinary use. It is absolutely immune against tarnish or corrosion in the air, and while it is not nearly so pliable as platinum, it can be worked into many of the forms used in jewelry without special difficulty. Finger rings can be made from it either in the plain form, or adapted to the Tiffany setting, so that it may be used in conjunction with any gem desired. If preferable, plain band rings can be made of the cast metal, which are practically file-proof, and at the same time possess a beautiful color and permanent luster.

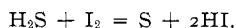
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THE INFLUENCE OF ADDED SUBSTANCES ON THE END-POINT IN THE IODOMETRIC TITRATION OF HYDROGEN SULFIDE

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INTRODUCTORY

Wide use is made of the reaction



in estimating the sulfur content of systems or materials containing this element either as hydrogen sulfide or as other compounds easily converted into hydrogen sulfide. Furthermore, such metals as zinc, cadmium,² etc., whose sulfides are readily soluble in acid, may be determined by isolating the sulfide, dissolving it, and titrating the resulting hydrogen sulfide with standard iodine.

The evolution methods of determining the sulfur content of irons and steels are in common use. The sample is dissolved in acid and the evolved hydrogen sulfide absorbed in a reagent whose nature is usually determined by whether the subsequent course of the analysis is to be a gravimetric, colorimetric or volumetric process. Numerous absorbents have been proposed,³

¹ The work reported in this article constitutes the basis of a thesis submitted by A. R. Jayson to the Faculty of the Graduate School of New York University, in part fulfillment of the requirements for the degree of Master of Science.

² von Berg, *Z. anal. Chem.*, **26** (1887), 23; Müller, *Bull. soc. chim.*, [4] **1** (1907), 13; Ibbotson and Aitchison, "Analysis of Non-Ferrous Alloys," **1915**, 168; Scott, "Standard Methods of Chemical Analysis," **1917**, 87.

³ Compilations and abstracts of the various proposals have been made by Brearley, *Chem. News*, **82** (1900), 306; Pulsifer, *THIS JOURNAL*, **8** (1916), 1119.

but those most generally employed in connection with the iodometric estimation of the hydrogen sulfide liberated are: sodium or potassium hydroxide; ammoniacal zinc solution or ammoniacal cadmium solutions. After absorption, these solutions or suspensions are made strongly acid and titrated with iodine in the presence of starch. The reaction between iodine and hydrogen sulfide takes place in the presence of a considerable quantity of acid and under these conditions the end-point is uncertain, for an excess of iodine is not made manifest by a sudden change from colorless to blue, but even in the early part of the titration the solution turns yellow, and passing through orange, red and purplish red, deepens; and forms a final purple instead of a pure blue. This difficulty may be overcome in part by standardizing the iodine solution by means of a sample of known sulfur content carried through the same procedure, but this is often inconvenient. It is better to add an excess of iodine to the acidified solution and titrate back with thiosulfate, as this gives a sharp end-point.

The appearance of the interfering colors is a matter of common knowledge and is usually ascribed to the presence of erythrodextrin or similar products of the hydrolysis of starch, though this is still an open question. Indeed, the real nature of the blue color produced by starch itself and iodine is still a matter of dispute.¹ Some have asserted that it is a mere physical phenomenon; others claim the existence of a definite compound, though the actual composition appears to vary with the concentration, temperature, etc., while still others view this as a case of adsorption. Harrison,² in particular, holds this latter view. He claims that the blue material is a colloidal suspension of iodine, starch acting as a protective colloid. He further states that starch, dextrins, starch-celluloses, etc., do not differ chemically but are merely different degrees of dispersion of the same substance. The various colors produced by these materials and iodine may be produced by addition of alcohol to aqueous starch iodide suspensions and *vice versa*; by warming and cooling; by addition of salts; processes which he holds merely change the degree of dispersion and consequently the protective action of the starch. As this decreases, iodine tends more and more to form true solution, and hence the color changes.

The influence of salts and other added substances upon the color produced by iodine and starch has been studied by Fresenius,³ Meineke,⁴ Pinnow,⁵ Lonnes,⁶ Burgstaller,⁷ and others. In general, salts increase the sensitiveness of the action and potassium iodide is particularly effective.⁸ However, excessive salt addition decreases the sensibility and often leads to changes in the starch so that yellows and reds appear when iodine is added. Meineke claims that large quantities of salts bring about a partial change of starch into materials less sensitive to iodine or into dextrins coloring red or yellow, *i. e.*, shades less noticeable than blue. Harrison ascribes this action of salts to changes in the degree of dispersion of starch. Hale⁹ found that ordinary starch contains as impurities, erythrodextrin, coloring red with iodine, and amidulin, coloring blue. The change of amidulin to erythrodextrin is catalyzed by potassium bicarbonate in the presence of an oxidizing agent and he thus explained the red

¹ Comments and references to the original papers may be found in Dammer, "Handbuch der anorganischen Chemie," **1** (1892), 549; **4** (1902), 229; Beilstein, *Ibid.*, **1** (1893), 1085; Suppl. I (1901), 588; Thorpe, "Dictionary of Applied Chemistry," **5** (1913), 157; Katayama, *Z. anorg. Chem.*, **56** (1907), 209.

² *Z. Koll. Chem.*, **9** (1911), 5; *Proc. Chem. Soc.*, **26** (1910), 252.

³ *Ann.*, **102** (1857), 184.

⁴ *Chem.-Ztg.*, **18** (1894), 157.

⁵ *Z. anal. Chem.*, **41** (1902), 485.

⁶ *Ibid.*, **33** (1894), 409.

⁷ *Chem.-Ztg.*, **36** (1912), 589.

⁸ Washburn, *J. Am. Chem. Soc.*, **30** (1908), 45; Treadwell and Hall, "Analytical Chemistry," **2** (1907), 513.

⁹ *Am. J. Sci.*, [4] **13** (1902), 379.

color appearing during the titration of arsenious acid with iodine in the presence of this compound.

We have assumed that the red color appearing during the titration of hydrogen sulfide is due to the presence of erythro-dextrin. The acid brings about the hydrolysis of starch but it ordinarily acts very slowly in the cold. The depth of color appearing during the titration carried out under the conditions being discussed indicates that the hydrolysis is catalyzed and we believe that hydrogen sulfide is the principal accelerator, functioning in acid solution somewhat as Hale found potassium bicarbonate to act in an alkaline medium. Our work was directed toward the discovery of a preventative of this hydrolysis and titrations were carried out in solutions of varying acid concentration and in the presence of numerous salts. None of these altered conditions brought about sufficient improvement in the end-point coloration to warrant adoption in technical practice, but the results were of enough interest to justify their appearance at this time.

EXPERIMENTAL

The solutions of iodine and thiosulfate used were $N/100$. Five cc. of a fresh solution containing 5 g. soluble starch (Lintner) per liter were used in each case. Preliminary tests showed that ordinary wheat and potato starch gave the same result. A fresh aqueous solution of hydrogen sulfide was used.

The conditions under which the interfering colors would form were first determined. Starch and iodine gave a pure blue; 25 cc. hydrogen sulfide solution diluted with 500 cc. water and titrated with iodine gave a blue end color and no preliminary reds. When, however, the hydrogen sulfide was diluted with 500 cc. water, 75 cc. hydrochloric acid (1 : 1) added and then titrated, a red color appeared almost immediately, growing deeper as the titration proceeded and finally changing to purple. The acid is necessary for the appearance of the red color, and, accordingly, tests were made using decreasing volumes of acid, the total volume of solution being kept constant by the addition of water. The results are given in Table I.

Hydrogen sulfide solution... 25 cc.		Starch paste..... 5 cc.	
No.	HCl (1 : 1) Cc.	H ₂ O Cc.	Color at End-point
1.....	0	575	Pure blue
2.....	5	570	Purplish blue
3.....	10	565	Purplish blue
4.....	15	560	Purple
5.....	25	550	Purple
6.....	50	525	Deeper red
7.....	75	500	Deeper red

The intensity of the red color increases with the acidity of the solution, and the interference of the pink with the blue is not very noticeable when less than 15 cc. acid is present: 0.02 g. cadmium sulfide was suspended in 500 cc. water, 15 cc. acid added, and the resulting hydrogen sulfide titrated with iodine. Although the red color was not very pronounced, the sulfide dissolved so slowly that the results were far from accurate. It is possible to add an excess of iodine to the suspension containing no acid, allow to stand for half an hour or so and then titrate the excess. This method has been recommended for the estimation of zinc.¹ However, if immediate results are desired, or if the use of a second standard solution is not convenient, it appears impracticable to reduce the acid to the point where the interference of the red is negligible.

Titrations were carried out in the presence of other acids. Sulfuric acid in quantities equivalent to the hydrochloric acid used above produced the corresponding red color, but the slightly dissociated acids, acetic and boric, gave no red during the titration and a pure blue end-point: 75 cc. of 15 per cent phosphoric acid in a total volume of 575 cc. gave a light pink, changing to a

purple end color, thus showing an intermediate behavior.¹ However, cadmium sulfide dissolves in acetic acid so slowly, even in the presence of iodine, that its use does not seem feasible. The effect of adding rather high concentrations of chlorides to the hydrochloric acid solution was studied in the hope that they would sufficiently depress the ionization of the acid to overcome the color formation. The results of adding saturated sodium chloride solution are shown in Table II.

Hydrogen sulfide solution 25 cc.		Hydrochloric acid (1 : 1) 75 cc.		Starch paste 5 cc.	
No.	NaCl (sat. sol.) Cc.	H ₂ O Cc.	Color at End-point		
1.....	0	500	Deep red		
2.....	50	450	Deep red		
3.....	100	400	Deep red		
4.....	200	300	Deeper red		

No improvement was noted: 500 cc. saturated sodium chloride solution containing 75 cc. acetic acid (20 per cent) gave a light red, changing to purple; 500 cc. saturated sodium acetate solution containing 75 cc. hydrochloric acid (1 : 1) gave a yellow, passing through reddish yellow to purple; 500 cc. saturated solution disodium hydrogen phosphate containing 75 cc. hydrochloric acid (1 : 1) gave a pink, changing to purple. These attempts to decrease the hydrogen ion content by addition of salts derived from weak acids had no favorable effects, and the hydrochloric acid present in these equilibria was sufficient to hydrolyze the starch. The results with 15 per cent calcium chloride solution are shown in Table III.

Hydrogen sulfide solution.... 25 cc.			Starch paste..... 5 cc.	
No.	15% CaCl ₂ Cc.	HCl (1 : 1) Cc.	H ₂ O Cc.	Color at End point
1.....	0	0	575	Blue
2.....	0	75	500	Deep red
3.....	25	75	480	Deep red
4.....	40	75	460	Deep red
5.....	60	75	440	Deep red
6.....	80	75	420	Deep red
7.....	100	75	400	Deep red
8.....	150	75	350	Deep red
9.....	200	75	300	Deep red

A repetition of these experiments, using 10 per cent, 20 per cent and saturated solutions of calcium chloride, showed no improvements. Meineke² noted that calcium chloride produced a red end color even when no acid was present; he found bismuthates to show the same tendency and even large concentrations of potassium iodide have the same effect. Titrations in the presence of varying concentrations of potassium chloride, sodium sulfate, magnesium sulfate, barium chloride and aluminum sulfate showed no reduction of the red color. Goppels-roeder³ found that magnesium sulfate, even in the absence of acid, tended to give red tints to the starch iodide coloration, while large amounts of potassium alum gave red colors exclusively.

Cadmium sulfide.....0.02 gram		Starch paste..... 5 cc.		
No.	NaCl (sat. sol.) Cc.	HCl (1 : 1) Cc.	H ₂ O Cc.	Color near End-point
1.....	0	75	500	Deep red
2.....	100	25	450	Deep red
3.....	150	25	400	Deep red
4.....	200	25	350	Deep red
5.....	300	25	250	Deep red

Cushman⁴ has shown that cadmium sulfide will dissolve in strong sodium chloride solutions containing low concentrations of hydrochloric acid. This seemed to offer a method of avoiding the undesirable effects of excess acid while permitting solution of the sulfide. The results are given in Table IV.

¹ Pinnow (*loc. cit.*) found acids to increase the sensitiveness of the iodo-starch reaction in the order of their electrical dissociation, but he points out that the H ion concentration is not the only factor involved since salts are often more effective than the corresponding acids.

² *Loc. cit.*

³ *J. Fort. Chem.*, 1868, 670; *Ann. Phys.*, 209, 57.

⁴ *Am. Chem. J.*, 17 (1895), 379.

¹ Pouget, *Compt. rend.*, [1] 129 (1899), 45.

Although solution of the sulfide still occurred when the volume of acid was reduced to 15 cc., one hour was required to complete the solution and titration. Less than this quantity of acid produced no appreciable solution of sulfide no matter how much sodium chloride was present. In no case was the red color reduced.

The failure of the coagulating electrolytes to bring about improvement indicates that the colloidal sulfur produced during the reaction is not responsible for the red coloration. Likewise, acidified solutions of thiosulfate containing sulfur in varying stages of aggregation gave pure blue end colors with no preliminary reds when treated with iodine. If a small quantity of hydrogen sulfide was added before beginning the titration, reds and purples appeared as soon as any thiosulfate still present had reacted. The starch and acid could be left in contact for a considerable period without influencing the end color. Titrations were made as usual except that the acid was not added until the end-point was almost reached, and when the few drops of iodine necessary to complete the reaction were added carefully no red appeared and the end color was pure blue. If the addition of the starch was deferred until just before the end-point was reached, the acid being present from the beginning, no interfering colors formed. If, in either of these cases, the solution was allowed to stand for some time before completing the titration, the end color was pure blue, if the last iodine was added slowly. If added rapidly, a faint pink appeared which deepened and gave way to a purple end color, and the faster the iodine was added, the deeper the red. The significance of this will be discussed later.

Although a deepening of the red color as the titration progresses is accompanied by an increase of both hydrogen iodide and sulfur, these materials probably exert no catalytic action, since titration of acidified suspensions of cadmium sulfide which slowly liberate the same total quantity of hydrogen sulfide as was present in 25 cc. of the aqueous solution, show a much deeper color even from the beginning than was observed with the aqueous solutions. It seems improbable that equal quantities of sulfur and hydrogen iodide should exert increased catalytic action, and as will be pointed out later, depth of color appears rather to be dependent on the local concentration of hydrogen sulfide. If hydrogen sulfide is the catalytic agent, why should the red color increase as it is progressively removed? When titrating aqueous solutions there is so much hydrogen sulfide present at the beginning that it reacts rapidly with the iodine and so prevents, to a great extent, the formation of the red erythro-dextrin iodide. As it is used up the erythro-dextrin has more opportunity to combine with the iodine and the red color deepens. No red at all appears when a concentrated solution of hydrogen sulfide is titrated, until its concentration is reduced to about that prevailing in our solutions. Furthermore, if the iodine is added slowly and the solutions thoroughly stirred after each addition, little if any permanent red appears as long as the concentration of the hydrogen sulfide is comparatively high. As the reaction progresses, it becomes increasingly difficult to remove the color by stirring, for now the erythro-dextrin has a chance to combine with the iodine. If the iodine is added rapidly, the red appears immediately and quickly deepens. Under these conditions the local concentration of hydrogen sulfide is not sufficient to react with all the iodine and erythro-dextrin iodide forms. The increased red observed when titrating a slowly dissolving sulfide may be due to the low local concentration of the hydrogen sulfide.

If the titration is carried past the end-point and then back-titrated with hydrogen sulfide, the solution becomes colorless. If more iodine is then added, the red reappears and gives a purple end color. If the first color is discharged with thiosulfate, the subsequent addition of iodine produces no red or purple but a pure blue. This difference is significant. Addition of

excess iodine and back-titration with thiosulfate leads to a sharp end-point and so this procedure has been recommended and we find this the only method giving constant agreement when titrating hydrogen sulfide solutions. Hale points out the following facts in explanation of this feature: Although starch will remove iodine from erythro-dextrin iodide, and form starch iodide, toward the end of the titration, an excess of iodine is present for a short time and both iodides are formed together. Although in alkaline solution, a reducing agent (sulfurous acid) fades the blue first, leaving the red to fade more slowly; in acid solution the red fades first and the blue last, even in the presence of an abundance of materials coloring red with iodine. This may explain why in the back-titrations with thiosulfate one is not bothered by the appearance of red hues.

We believe that the erythro-dextrin is formed at the point of reaction of the iodine and hydrogen sulfide and the resulting relatively high local concentration of erythro-dextrin permits the formation of the red material, if the concentration of hydrogen sulfide at this point is not too great. This conclusion is analogous to that arrived at by Hale who found that potassium bicarbonate catalyzes the change of amidulin to erythro-dextrin only in the presence of an oxidizing agent. In the same way we believe the hydrogen sulfide accelerates the hydrolytic action of the acid in the presence of iodine. Hale found that starch prepared according to Zulkowsky¹ gave no interfering colors. We prepared a sample of this "amorphous amylo-dextrin," which, when tested in the iodometric titration of an arsenite in the presence of potassium bicarbonate gave a pure blue end color. When used as indicator during the titration of hydrogen sulfide in acid solutions, this pure starch showed slightly less red, but the end color was purple and the exact end-point as uncertain as when ordinary starch was used.

CONCLUSIONS

The following hypothesis is advanced to account for the red color appearing during the iodometric titrations of hydrogen sulfide in acid solution: the acid hydrolysis of starch to erythro-dextrin is accelerated by hydrogen sulfide in the presence of iodine. This hydrolysis occurs at the point at which iodine and hydrogen sulfide react, and though, at ordinary concentrations, iodine reacts with hydrogen sulfide and combines with starch in preference to erythro-dextrin, under conditions of high local concentration erythro-dextrin iodide may also be formed. At the end of the titration the formation of erythro-dextrin no longer occurs, blue starch iodide forms, and a mixture of the latter and the red erythro-dextrin iodide already present gives a purple end color. On standing, the erythro-dextrin iodide gives up its iodine to the starch, and the purple changes to a pure blue, but this final color change proceeds too slowly to be of practical significance.

SUMMARY

I—The conditions leading to the red color appearing during the titration of hydrogen sulfide with iodine in acid solution have been studied and an hypothesis advanced to account for the phenomenon.

II—The quantity of erythro-dextrin formed (depth of the red color) is dependent on the nature of the acid present and its formation increases with rising concentration of acid. Reduction of the concentration of acid beyond a certain point is impracticable when titrating cadmium sulfide suspensions because of the slow rate of solution.

III—The addition of various salts has not made the end-point more definite.

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¹ *Ber.*, **13** (1880), 1395.