

TABLE IV.—TEST SERIES CONTAINING SILICA.

Gram magnesium.		Parts Mg per million of solution.	
Present.	Found.	Present.	Found.
0.000316	0.000313	6.32	6.26
0.000316	0.000316	6.32	6.32
0.000158	0.000147	3.16	2.94
0.000158	0.000151	3.16	3.02
0.000079	0.000094	1.58	1.88
0.000079	0.000088	1.58	1.76
0.000040	0.000055	0.80	1.10
0.000040	0.000054	0.80	1.08

The results clearly show that the silica has been entirely removed in the washing process.

The practical handling of the method as routine work by the assistants in charge of the investigations requiring the accurate determination of small amounts of magnesium has proven very satisfactory and expedient. With proper attention to details one man is able to make twenty determinations, including all calculations, in a working day of seven hours.

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## THE ESTIMATION OF SMALL AMOUNTS OF FERRIC IRON BY ACETYLACETONE (ESPECIALLY APPLIED TO WATER ANALYSIS).

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It is less than twenty years ago that Combes<sup>1</sup> first prepared acetylacetone and its metallic salts. He mentioned that acetylacetone gives an intense red coloration with ferric salts.

The following was undertaken to ascertain the limits and conditions attending this color reaction, and to compare its value with that of other reagents commonly used to estimate iron qualitatively and quantitatively.

Acetylacetone is a colorless liquid, boiling at 137°. Combes showed its structure to be  $\text{CH}_3\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3$ . One of the hydrogen atoms attached to the middle carbon atom is easily replaceable by the common metals.

<sup>1</sup> *Compt. Rend.*, 105, 868.

To prepare the metallic acetylacetonates we have the simple procedure of treating the metallic hydroxide with acetylacetone and crystallizing from alcoholic solution.

Ferric acetylacetonate is, accordingly, made by shaking ferric hydroxide with an alcoholic solution of acetylacetone. On concentrating or cooling the hot saturated solution the salt separates in handsome dark red crystals. The streak of fine powder is a clear orange-red. Solutions containing ferric ions and acetylacetone react immediately to form the colored salt. If there be much of the salt present, the color is deep red by transmitted and orange-red by reflected light. More dilute solutions are orange-red by transmitted and yellow by reflected light.

In its water solution it is probably only very slightly dissociated, as shown by the conductivity measurements made by Hantzsch and Desch.<sup>1</sup> It is, however, largely hydrolyzed into ferric hydroxide and acetylacetone. Its saturated water solution, made by shaking excess of the substance with water for twenty-four hours, contained 1.5 grams per liter in solution. Gravimetric determination by evaporating and weighing as  $\text{Fe}_2\text{O}_3$  gave 1.48 grams. Colorimetric determination against standard solutions gave 1.5 grams. Urbain and Debierne<sup>2</sup> reported it to be almost insoluble in water. On evaporating its solution on a water-bath only ferric hydroxide remains to form the residue. That the water solution is largely hydrolyzed may be inferred from the fact that, while the addition of either acetylacetone or ferric ions to a saturated solution deepens the color, the addition of an acid causes a very great increase in the color. Rosenheim and Cohn<sup>3</sup> have studied the similar behavior of ferric sulphocyanate. In our case the amount of associated ferric acetylacetonate in the saturated solution was found to be only 25 per cent. The determination was carried out as follows: Fifty cc. of the saturated solution were put directly into a shallow tube so that the color could be read without difficulty on looking down through the highly colored liquid. Into another tube was put an excess of acetylacetone and the volume made slightly less than that of the liquid in the first tube by pouring in distilled water. A standard iron solution, which was slightly acid, was now added to the second tube until the colors

<sup>1</sup> *Ann. Chem.* (Liebig), **323**, 1 (1902).

<sup>2</sup> *Compt. Rend.*, **129**, 302.

<sup>3</sup> *Ztschr. anorg. Chem.*, **27**, 280.

matched. This last solution, containing excess of acetylacetone and free acid, would have all its ferric acetylacetonate in the associated condition. The colors matched when 3 cc. of a standard solution containing 0.001 gram iron per cubic centimeter had been added. This calculated to ferric acetylacetonate gives 0.00038 gram per cubic centimeter in the saturated solution. To determine the total iron present in the saturated solution, 2 cc. were transferred to a Nessler tube, excess of acetylacetone and a drop of dilute hydrochloric acid added and the color compared with standard cold tubes, already made up. This gave the total amount of iron present as 0.000235 gram per cubic centimeter. Its value as acetylacetonate is 0.0015 gram. We then have ferric acetylacetonate, as such, 0.00038 gram per cubic centimeter. Total iron and acetylacetone in solution, 0.0015 gram per cubic centimeter. Amount of association, 25 per cent. From the fact that the salt is so largely hydrolyzed in solution comes the chief difficulty in using it for the estimation of iron. It is possible, however, to get uniform results by taking the proper precautions as to the amount of acid present.

The delicacy, range, influence of other substances, influence of heat and permanency was, in each case, determined on solutions made up in common 50 cc. Nessler tubes. For this purpose the required amount of standard iron solution was measured into the tube, the reagent added, the tube filled with distilled water to the mark and the contents mixed by twice pouring into a clean tube. Colors could then be read immediately.

The acetylacetone used was Kahlbaum's, freshly distilled, and diluted with water or weak alcohol until it contained only 0.5 per cent. acetylacetone. Two cc. of this 0.5 per cent. solution added to the Nessler tube will furnish sufficient excess of the acetylacetone for as large amounts of iron as can be estimated by this method. Commercial acetylacetone darkens on standing, but distills colorless on the first distillation.

Standard iron solutions of various strengths were made by dissolving 99.98 per cent. iron wire in a few cubic centimeters of hydrochloric and nitric acids. These were then diluted to the required volume. The final solution should not contain so much acid that when it is made up in the Nessler tube for reading it looks pink by reflected light. Standard solutions may also be made

by weighing out ferrous ammonium sulphate and oxidizing before dilution, but, as before, the solution must be only faintly acid at the final dilution.

The least amount of iron that can be detected with acetylacetone is less than that which can be detected by potassium sulphocyanate, as it is commonly used. The following will illustrate the comparison:

STANDARD IRON SOLUTION, 1 CC. =: 0.000001 GRAM Fe.			
By pipette. cc.	Gram Fe.	2 cc. acetylacetone (0.5 per cent.)	5 cc. KSCN (0.5 per cent.)
1	0.000001	No color.	No color.
2	0.000002	"	"
3	0.000003	Distinct color.	"
4	0.000004	Darker.	"
5	0.000005	"	"
6	0.000006	"	Faintest pink.

Under these conditions the smallest amount of iron that can be detected with acetylacetone is thus 0.000003 gram. The least that can be detected with sulphocyanate is 0.000006 gram. This does not mean that acetylacetone is the most delicate test for iron, but that, under these conditions, it is more delicate than the sulphocyanate. If 5 grams of potassium sulphocyanate are added to one of the tubes containing 0.5 cc. of the above standard solution it will give a distinct pink color. This is 0.0000005 gram of iron in 50 grams of substance. Again, one drop of the same solution, which will contain about 0.04 cc., will be colored distinctly pink if a crystal of solid potassium sulphocyanate is applied. This is a detection of 0.00000004 gram of iron. Experiments made to have acetylacetone detect less than 0.000003 gram of iron were not successful.

The reaction with salicylic acid in the Nessler tube has a sensitiveness quite similar to that of the sulphocyanate, but the color fades rapidly. The reaction with potassium ferrocyanide is not nearly so delicate and the reagent has the disadvantage that it has a strong color of its own.

The range over which acetylacetone is available is somewhat greater than that of the sulphocyanate. The smallest amount that can be detected has already been stated to be 0.000003 gram. The largest amount that can well be estimated in the 50 cc. tube is about 0.0006 gram. Excepting for the smaller amounts, the total amount present can be estimated to at least one-tenth of the

amount present; from 0.00005 gram to 0.0006 gram the accuracy is even better. For instance, if the solution contains about 0.00005 gram, it is not difficult to detect a variation of 0.0000025 gram, and for amounts of about 0.0004 gram it is not difficult to detect variations of 0.00001 gram. Under the same conditions the color produced by sulphocyanate becomes difficult to read, if the tube contains 0.0003 gram iron.

Very few common inorganic salts that can exist in solution with ferric iron have any influence on the color when present in small amounts.

Substances to the amount of 0.2 gram, which will furnish the following ions, have no effect whatever: Na, K, Ca, Sr, Ba, Cl, Br,  $\text{SO}_4$ ,  $\text{NO}_3$ ,  $\text{ClO}_3$ , Mg, Zn, Pb, Mn, As, Cd, Al and Hg.

Smaller amounts of silicic acid, phosphoric acid and copper do not interfere. Carbon dioxide in solution has no influence. The acetylacetonate may be used in water or alcoholic solution, the presence of alcohol not altering the color. Oxides of nitrogen give a brown color with acetylacetonate and should be removed from the concentrated solution by boiling. Caustic soda or potash destroys the color and precipitates iron from its solution of ferric acetylacetonate. The iron is not precipitated by ammonia; ammonia gives a strong yellow color to the solution, although the iron can still be estimated by its characteristic color.

Ferric acetylacetonate acts as an indicator, its neutral orange-red solution turning pink with acids and yellow with ammonia. It is not a delicate indicator, hence it can be used for the estimation of iron either in faintly acid solutions, when its color is brown or red; or it can be used in stronger acid solution when its color is a clear pink; or it can be used in solutions distinctly alkaline with ammonia when it has a yellow hue. Solutions once distinctly pink change only slightly on addition of small amounts of acid, but for the best work in pink solutions the amount of acid in all the solutions compared should be uniform. Solutions once distinctly alkaline to litmus with ammonia do not have their color changed by the addition of more ammonia. Considerable variation in the amount of acid may be allowed in the original solution, provided that it is sufficiently diluted before the acetylacetonate solution is used. The final 50 cc. Nessler tube should not contain enough acid to have the tube look pink when viewed from the side. The original solution may well contain less than 10 cc. of any dilute

acid. This should then be diluted to 500 or 1000 cc. and portions as small as needed then transferred to the Nessler tube. for under the conditions of faintly acid solution scarcely more than a drop of any one of the common dilute acids is permissible in the Nessler tube. The addition of even one drop of a strong acid to a faintly acid tube weakens and changes the color, two drops has a greater influence and ten drops may remove nearly all the color.

If the original substance contains more than a trace of iron, the final dilution for the best readings of iron will have diluted the other material present so much that it will no longer be present in sufficient quantity to interfere with the accuracy of the determination. If the solution does contain sufficient acid to be pink, it will, of course, be necessary to influence the standards likewise.

There is one serious objection to the use of potassium sulphocyanate for the quantitative estimation of iron; the color first produced immediately begins to fade and continues to fade. An hour's exposure to sunlight will render a solution originally a deep red almost colorless. The color decreases during an hour even in the dark, and considerably more rapidly in diffused light. This is a source of serious error unless great care is used and even then it is a source of constant annoyance. The cause of the fading has been given by Shilton<sup>1</sup> to be due to the reducing action of the sulphocyanate. The color produced by salicylic acid also fades so rapidly that the faintly colored solutions soon lose all color.

The permanency of the color produced by acetylacetone and ferric ions in the faintly acid solutions adds greatly to the usefulness of this reagent. Tubes so faintly acid as to have the brownish or orange-red hues by transmitted and yellowish hues by reflected light showed remarkable permanency. Tubes freshly made up compared exactly with ones made up an hour or even three weeks previously. Strong sunlight altered the hue somewhat. Tubes strongly pink with acid showed some fading on standing a day.

Changes of temperature over small ranges have no appreciable effect on the color of ferric acetylacetonate. Boiling will remove the greater part of the color from a solution red with sulphocyanate. Boiling changes the hue of the solution red with acetylacetone, but the change is only temporary and the original color is resumed on cooling.

<sup>1</sup> *Chem. News*, 234 (1884).

This test for iron can be used in all those places where potassium sulphocyanate has been used. In nearly all cases where it is to be used sufficient dilution for the best readings of the iron will also so dilute the other salts present that they will not interfere with the estimation of the iron. In all cases the residue containing the iron may be taken up in a very few drops of nitric or hydrochloric acid, or both, and largely diluted. An aliquot part of this solution is then transferred to the Nessler tube and the estimation made.

For water analysis, either 100 cc. of the water may be evaporated to dryness on the water-bath and all organic matter removed by sulphuric and nitric acids, or the residue from the total solids may be used. The ferric oxide left from the ignitions is insoluble in nitric acid and is dissolved with difficulty by hydrochloric acid. However, it yields to warming with a few drops of dilute sulphuric acid and a drop of hydrochloric acid.

If much insoluble residue is now present, the solution may be filtered through a very small filter into a porcelain dish. After washing the filter, the iron may all be oxidized by a few drops of hydrogen peroxide or dilute nitric acid. If only traces of iron are present, the solution may be evaporated almost to dryness to expel the excess of acid, transferred to a Nessler tube, 2 cc. of 0.5 per cent. acetylacetone added and the solution made up to the mark with distilled water. If larger amounts of iron are present, the small amount of acid may not need to be removed by evaporation, but the solution diluted to 500 cc. or 1000 cc., and a definite portion of this transferred to the Nessler tube, 2 cc. of acetylacetone solution added and the tube filled to the mark with distilled water. The contents of the tube should finally be thoroughly mixed by twice pouring into a clean tube or beaker.

For occasional analyses standards may be made by preparing the sample, then making the standard to match by putting the 2 cc. of acetylacetone into a tube, partly filling with water, and then adding sufficient standard iron solution to match the sample tube after filling to the mark with water and thoroughly mixing.

For continuous use, standards may be prepared from varying strengths of standard iron solution and kept free from dust and away from direct sunlight.

In no case should colors be matched by pouring out one solution and estimating the iron by the color of the fractionally

matched tubes. Experiments proved that it does not follow that pouring out half of the solution from a tube will leave a color at all comparable with the regular tube containing half the amount of iron. For accurate work the conditions as to acid, excess of acetylacetonc and volume should be the same.

*Summary.*—Of all the reagents that have been used for the quantitative estimation of ferric iron, potassium sulphocyanate has been the most satisfactory. A real source of weakness has been the loss of color attendant on standing for even brief intervals.

Acetylacetonc is a reagent equally sensitive under usual conditions; it has greater range; there are almost no substances which interfere when they are present in small amounts, while the color produced in faintly acid solutions has a very considerable permanency.

#### REFERENCES TO THE COLORIMETRIC ESTIMATION OF IRON.

Early mention of KSCN as a qualitative test: Henry Ossian, *Pharmaceutisches Central-Blatt*, p. 205 (1837).

Delicacy of different tests: Vogel, Aug. (Salicylic Acid), *N. Rep. Pharm.*, 25, 180 and *Chem. Centrbl.*, p. 375 (1876); Pagliani, S. (Salicylic Acid), *Gazz. chim. ital.*, 9, 23, and *J. Chem. Soc.* (London), abst. 748 (1879); Smith, E. E. (KSCN and Salicylic Acid), *Proc. Am. Phil. Soc.*, 18, 214 and this Journal, 1, 335 (1879); Wagner, A. (Ferrocyanide, KSCN, Tannin), *Ztschr. anal. Chem.*, 20, 349 (1881); Thompson, A. (KSCN), *J. Chem. Soc.* (London), p. 493 (1885); Venable, E. F. (Cobalt Nitrate), *J. Anal. Chem.*, 1, 312 and *Chem. Centrbl.*, 1, 185 (1887).

Iron in waters: By KSCN—Herapath, T. J., *J. Chem. Soc.* (London), p. 27 (1853); Davies, J., *Chem. News*, p. 163 (1863); Zega, A., *Chem. Ztg.*, 17, 1564 and *J. Chem. Soc.* (London), abst., p. 215 (1894); Seyda, A., *Chem. Ztg.*, 22, 1085 (1898); *J. Chem. Soc.* (London), abst., p. 341 (1899). By Ferrocyanide—Carnelly, T., *Chem. News*, 30, 257 (1874); *J. Chem. Soc.* (London), 285 (1895); Bell, J. C., *J. Soc. Chem. Ind.*, 8, 175 (1889); *J. Chem. Soc.* (London), abst., p. 419 (1890). By Tannin—Gerhard, F., *Arch. Pharm.*, 230, 705 and *Chem. Centrbl.*, i, 366 (1893); Ewers, E., *Apoth. Ztg.*, 13, 536; *Chem. Centrbl.*, ii, 605 (1898); *J. Chem. Soc.* (London), abst., p. 252 (1899). By Ammonium Sulphide—Sabanejeff and Kislakowsky, *Pharm. Ztg. Russ.*, 26, 776; *J. Chem. Soc.* (London), abst., p. 108 (1888); *Chem. Centrbl.*, 84, (1888); Winkler, L. W., *Ztschr. anal. Chem.*, 41, 550 (1902); *J. Chem. Soc.* (London), abst., p. 108 (1903); *Chem. Centrbl.*, ii, p. 1343 (1902).

Iron in blood: Lapicoue, L., *Compt. Rend. Soc. Biol.*, p. 669 (1890) and *J. Chem. Soc.* (London), abst., p. 240 (1892); also *Bull. Soc. Chim.* (3), 2, 295; *J. Chem. Soc.* (London), abst., p. 297 (1890).

Iron in chemicals: Battger, R. (Nickel Salts), *J. Chem. Soc.* (London), abst., p. 1101 (1874); *Chem. Centrbl.*, abst., p. 407; Griggi, G. (Copper Sulfate), *Ztschr. anal. Chem.*, 34, 450 (1895); *J. Chem. Soc.* (London), abst., p.



534 (1895); Lunge, G. (Aluminum Sulphate), *Ztschr. angew. Chem.*, 3 (1896); *J. Chem. Soc.* (London), abst., p. 392 (1896); Tatlock, R. R. (Alum), *J. Soc. Chem. Ind.*, 6, 276 (1887); *J. Chem. Soc.* (London), abst., p. 90 (1888).

Iron in minerals: Johnstone, A., *Chem. News*, 231 (1889).

Iron in wines: Borntraeger, A., *Chem. Ztg.*, 20, 398 (1896); *Chem. Centrbl.*, p. 207 (1896); *J. Chem. Soc.* (London), abst., p. 233 (1897); Ewers, E. (See Iron in Waters).

Ferric iron and potassium sulphocyanate: Werner, H., *Ztschr. anal. Chem.*, 22, 44 and *J. Chem. Soc.* (London), abst., p. 510 (1883); Shilton, A. J., *Chem. News*, p. 234 (1884); *Chem. Centrbl.*, p. 487 (1884); Krüss and Moraht, *Ann. Chem.* (Liebig), 260, 202 and *Chem. Centrbl.*, p. 738 (1889); *Chem. Centrbl.*, p. 808 (1889); *J. Chem. Soc.* (London), abst., p. 1129 (1889); *Ibid.*, abst., p. 1247 (1889); Magnanni, G., *Ztschr. phys. Chem.*, 8, 1 (1901); *Chem. Centrbl.*, ii, p. 613 (1901); Ribau, J., *Bull. Soc. Chim.* (3), 6, 916 and *J. Chem. Soc.* (London), abst., p. 1132 (1891); *Bull. Soc. Chim.* (3), 7, 199 and *J. Chem. Soc.* (London), abst., p. 50 (1893); Krüss and Moraht, *Ztschr. anorg. Chem.*, 1, 399 and *J. Chem. Soc.* (London), abst., p. 185 (1893); Gladstone, J. H., *Chem. News*, 67, 1 and *J. Chem. Soc.* (London), abst., p. 289 (1893); Schultze, H., *Chem. Ztg.*, 17, 2 and *J. Chem. Soc.* (London), abst., p. 438 (1893); Veron, H. M., *Chem. News*, 66, 177, 191, 202, 214 and *J. Chem. Soc.* (London), abst., p. 122 (1893); Ley, H., *Ztschr. phys. Chem.*, 30, 193 (1899); Rosenheim and Cohn, *Ztschr. anorg. Chem.*, 27, 280 and *Chem. Centrbl.*, 2, 199 (1901).

Ferric acetylacetonate: Combes, A., *Compt. Rend.*, p. 105 and *J. Chem. Soc.* (London), abst., 128 (1888); Urbain and Debiegne, *Compt. Rend.*, 129, 302 (1899); *J. Chem. Soc.* (London), abst., p. 789 (1899); Hantzsch and Desch, *Ann. Chem.* (Liebig), 323, 1 (1902); *J. Chem. Soc.* (London), abst., p. 708 (1902).

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## DETERMINATION OF PHOSPHATES IN NATURAL WATERS.

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THE potability of water is impaired by the presence of decaying organic matter. In this process of decay one of the numerous changes produced is the conversion of organic phosphorus compounds into phosphates. But the presence of phosphates does not necessarily indicate a source of contamination, because they may also be present as a result of waters charged with carbonic acid percolating through the rocks and minerals. Particularly in the case of streams and shallow wells the water may contain a large amount of phosphates derived from the fertilizers being used on