In the above experiments successively larger amounts of lead chloride have been added.

In our experience the quantity of ammonium chloride necessary to have present can be anywhere from 1 to 20 grams in a 200 cc. solution. When excessively large amounts are present, 40 grams or more, the endpoint becomes indistinct.

Various indicators have been suggested from time to time to determin the endpoint in the ferrocyanide titration for zinc. Our experiments suggest that a 0.9% ammonium molybdate solution is the most delicate of the various indicators proposed, but that it is not widely applicable. Glacial acetic acid, 5% sodium tungstate, cobalt nitrate, hydrochloroplatinic acid, are fair indicators, but not as delicate as uranium nitrate or ammonium molybdate. Of all the indicators used, the 5% solution of uranium nitrate is very delicate and reliable.

Conclusions.

In the ferrocyanide titration for zinc as commonly carried out, lead is without influence.

The ferrocyanide titration for lead should be carried out in acetic acid solution and the mineral acids must be absent.

In the technical examination of ores for zinc where lead and iron are the only heavy metals present to an appreciable extent, and such is the case with the Wisconsin zinc ores, it is unnecessary to remove the lead for the ferrocyanide titration for zinc. Half-gram samples of the ore can be dissolved in 10 cc. of concentrated hydrochloric acid with the addition of a little nitric acid. To the solution after dilution, ammonium hydroxide is added and the ferric hydroxide and insoluble matter are removed by filtration. The precipitate is dissolved in dilute hydrochloric acid and reprecipitation by ammonia is effected, the filtrates being united. The solution should now be acidified with hydrochloric acid and when evaporated somewhat is ready to be titrated.

For titration the solution must be hot, it should have a volume of 200 cc., should contain 6–10 cc. concentrated hydrochloric acid and 10 grams of ammonium chloride. The ferrocyanide solution should be of such strength that 1 cc. = 0.005 gram zinc, and the best indicator is a 5% solution of uranium nitrate.

MADISON, WIS.

A NEW COLORIMETRIC METHOD FOR TITANIUM.

BY VICTOR LENHER AND W. G. CRAWFORD.

Received December 10, 1912.

The estimation of titanium is commonly considered by chemists as one of the more troublesome determinations. The methods most widely used exemplify two distinctly different types of chemical action, namely, hydrolysis and colorimetric comparisons. With high percentages of titanium, the hydrolysis of the sulfate is one of the oldest gravimetric methods. The substitution by Gooch[1] and Chatard[2] of acetic acid solution for that of the sulfate affords a solution for hydrolysis which gives a far more satisfactory method of separation and precipitation than the older sulfate method. Baskerville's[3] method of hydrolysis in hydrochloric acid has been repeatedly tried out in this laboratory with titanium-bearing material carrying very low percentages up to pure rutile, and uniformly excellent results have been obtained as compared with the acetate method.

For low percentages of titanium the colorimetric method first proposed by Weller[4] is most generally applicable. The method is based on the yellow color produced when hydrogen peroxide is added to a sulfuric acid solution of titanium. This colorimetric method has found great applicability in the analysis of clays, silicate rocks and material of this general character low in titanium. The sensibility of the color to the presence of fluorides is so pronounced that this bleaching action on a titanium solution containing hydrogen peroxide has been proposed by Steiger[5] as a means of estimating fluorides.

Levy,[6] in studying some color reactions of titanic, columbic, tantalic and stannic acids, found that certain organic compounds containing one or more phenol groups gave deep colorations with these acids. He worked in concentrated sulfuric acid solutions and observed that all of the colorations were destroyed by the addition of a small quantity of water, with the exception of those produced by stannic acid. From the results obtained he suggested a qualitative method for those acids and conversely a method for the detection of certain phenols.

Muller[7] has studied the colorimetric determination of titanium in aqueous solution by means of the color imparted by salicylic acid, and finds that the detection of very small amounts of titanium is thus made possible.

In studying the double fluorides of columbium, titanium, tantalum and tungsten with various reagents in concentrated sulfuric acid, Hall and Smith[8] give a number of color reactions for titanium.

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[1] *Chem. News*, **52**, 55, 68 (1885).

[2] *Am. Chem. J.*, **13**, 106 (1891).

[3] THIS JOURNAL, **16**, 427 (1894).

[4] *Ber.*, **15**, 2593 (1882). See also *Z. anal. Chem.*, **9**, 41, 330.

[5] THIS JOURNAL, **30**, 219 (1907).

[6] *Compt. rend.*, **103**, 1075, 1195.

[7] THIS JOURNAL, **33**, 1506 (1910).

[8] *Proc. Am. Phil. Soc.*, **44**, 196 (1905).

TABLE I.

Morphine	Crimson	Salicylic acid	Deep red
Codeine	No color	Meta oxybenzoic acid	Chrome yellow
Brucine	Light red	Para oxybenzoic acid	Chrome yellow
Phenol	Brick red	Gallic acid	Brick red
α-Naphthol	Green to green brown	Cinchonidine	No color
β-Naphthol	Coffee brown	Apomorphine	Light red brown
Thymol	Garnet	Narceine	Brown
Resorcin	Red brown	Bebeerine	Clear brown
Hydrochinon	Crimson	Narcotine	Brown
Pyrocatechin	Chocolate	Chromotropic acid	Deep red
Pyrogallol	Dark red brown		

Continuing this line of study a number of other substances have been studied with regard to their behavior with titanium in strong sulfuric acid solution with the following results:

TABLE II.

Reagent.	Color produced in 1 minute.	Color produced in 24 hours.
Codeine	Light amethyst	Darker
Homatropine	Light red	Cherry
Hydrastine	Light pink	No change
Hyoscyamine	Dark brown	No change
Pelletierine	Light yellow	Pink
Physostigmine	Red	No change
Physostigmine salicylate	Rose yellow	No change
Piperine	Brown	Charred
Strophanthine	Light brown	No change
Aspidospermine	Red	No change
Avenin legumin	Chocolate	No change
Belladonnine	Deep red	Chocolate
Bulbocapnine	No color	Pink
Colchicine	Yellow, then red	Reddish brown
Collidine	Light brown	No change
Cryptopine	Deep purple	Black
Chelidonine	Deep red	Purple
Chlorogenine	Yellow	Light brown
Conessine	Light yellow	Dark yellow
Colchicine	Yellow	No change
Cotarnine	Red	No change
Delphinine	Dark red	Darker
Duboisine	Pink	Light reddish brown
Erythrophleine	Light red	Darker
Ditamine	Pink	Red
Digitalein	Red	Darker
Emetine	Red	Deep red
Hydrocotarnine	Red	Black
Jaborine	Red	Dark red
Jervine	Brown	Dark green
Lepidine	Light yellow	No change
Pelletierine	Light red	No change
Pseudopelletierine	Light yellow	No change
Daturine	No color	Pink

No colors are caused by atropine, caffeine, cinchonidine, pilocarpine, cinconine, cocoaine, quinine, scopolamine, sparteine, arecoline, anagyrine, cocaethyline, cinchonamine, conhydrine, cysisine, gelseminine, ecgonine, gussospernine, hyoscine, choline, lobeline, tritopine, tropine, taxine, laudanosine, lycoctonine, oxyacanthine, oxysparteine, picoline, protopine, papaverine, quebrachine, sabadilline, sabadine, aporetin, either in one minute or on being allowed to stand 24 hours.

The colorations produced by many of the substances worked with are so much more intense than the hydrogen peroxide color that a number have been tested to ascertain whether the color is proportional to the amount of titanium present and not affected by an excess of the reagent.

Phenol and titanium in sulfuric acid solution give a deep red color in strong solution and a yellow red in dilute. A series of experiments were carefully carried out with phenol and titanium in concentrated sulfuric acid solution, and although a color developed with as small an amount of titanium dioxide as 0.00005 gram, in no case was it found possible to get a solution in which the color is proportional to the amount of titanium present.

A similar series of experiments carried out with hydroquinone and titanium in concentrated sulfuric acid showed that, while it is possible to detect 0.0001 gram of titanium dioxide by this method, hydroquinone is not a satisfactory reagent for the determination of titanium.

Chromotropic acid in concentrated sulfuric acid solution was similarly found to show the presence of 0.00001 gram of titanium dioxide, but the color produced is not a function of the amount of titanium present.

Salicylic acid in concentrated sulfuric acid solution will indicate as small a quantity of titanium dioxide as 0.00001 gram, but here again the color is not proportional to the amount of titanium present.

A number of alkaloids were likewise tested with titanium in sulfuric solution, and while a number of them showed intense color reactions, none were found in which the color produced is proportional to the amount of titanium present.

Thymol and titanium in concentrated sulfuric acid solution give a deep red coloration if sufficient titanium is present, while in dilute solution a reddish yellow color is developed. The color produced by the addition of a sulfuric acid solution of titanium is proportional to the amount of the latter present and can be made the basis of a colorimetric determination.

Thymol dissolves in concentrated sulfuric acid with a slightly yellow color, which rapidly intensifies as the amount of thymol is increased. This coloration can be avoided if the thymol is first dissolved in a little acetic acid in which thymol is very soluble, or in acetic acid containing 10% of alcohol. Sulfuric acid can then be added without the formation of any color. The solution of thymol in sulfuric acid thus prepared is fairly stable and if kept out of bright light will not discolor, but if exposed to direct sunlight it will darken in a few hours.

The ratio of thymol to titanium can vary greatly, but it has been found best to have at least 0.006 gram of thymol present to every 0.0001 gram TiO_2.

Table III indicates results obtained in a Soleil-Duboscq colorimeter.

TABLE III.

No.	TiO_2 present. Mg.	TiO_2 found. Mg.
1	0.21	0.20
2	0.21	0.19
3	0.31	0.30
4	0.31	0.294
5	0.40	0.405
6	0.40	0.37
7	0.50	0.50
8	0.50	0.52

Table IV represents results obtained on somewhat larger quantities of titanium with a Kennicott-Sargent colorimeter.

TABLE IV.

No.	TiO_2 present. Mg.	TiO_2 found. Mg.
9	1.0	0.9
10	1.5	1.5
11	2.1	2.0
12	2.5	2.5

Four previously analyzed samples of bauxite in which the titanium content had been obtained by the Weller method, are compared in Table V with the thymol method. Samples of 0.3 gram each were fused with potassium bisulfate for a half hour, after which the fusion was taken up in concentrated sulfuric acid.

TABLE V.

No.	Weller's method.	Thymol method.	Thymol method.
13	3.3% TiO_2	3.7% TiO_2	3.4% TiO_2
14	1.93	2.2	2.1
15	2.20	2.15	2.28
16	2.97	2.83	2.95

Effect of Dilution.

Levy noted, when water is added to a titanium solution colored by thymol, that the color fades and is essentially destroyed. The following experiments indicate the effect of the dilution of the acid on the apparent percentage of titanium. Five hundred cc. of a standard titanium dioxide solution were prepared with an excess of thymol present. Aliquot portions were taken and a known amount of water was added to each portion. These portions were cooled and diluted to 50 cc. by the addition of sulfuric acid, sp. gr. 1.84. These test solutions were compared in turn with a 25 cc. portion of the original solution, diluted to 500 cc. with sulfuric acid, sp. gr. 1.84. The addition of water has apparently no effect on the color until a concentration of 79.4% (sp. gr. 1.725) sulfuric acid has been reached, after which the color fades in a perfectly regular manner. It has been necessary in making this dilution study to cool the solutions to room temperature after the dilution of the acid, inasmuch as a warm solution is much lighter in color than one of the same strength a few degrees cooler.

TABLE VI.

Per cent H_2SO_4.	Actual TiO_2 present. Mg.	Apparent TiO_2 present. Mg.	Apparent TiO_2 present. Per cent.
90.05	0.625	0.625	100
87.60	0.625	0.625	100
85.70	0.625	0.625	100
83.32	0.625	0.625	100
82.00	0.625	0.625	100
80.68	0.625	0.625	100
79.36	0.625	0.625	100
77.60	0.625	0.575	92
76.30	0.625	0.537	86
74.51	0.625	0.500	80
73.23	0.625	0.462	74
71.99	0.625	0.412	66
70.74	0.625	0.375	60
68.97	0.625	0.337	54
67.59	0.625	0.300	48

Effect of Temperature.

The fact that a titanium solution colored by thymol loses some of its color when heated and that on cooling the color returns, has been repeatedly observed. A series of experiments was therefore conducted to determin at how high a temperature such a solution could be heated without change of color. In each case the solution was heated to the temperature noted, after which it was cooled and compared with a sample of the original solution. It has been found that the color is not permanently changed until the solution is heated to 100°.

TABLE VII.

No.	Room temperature.	Temperature of heating.	TiO_2 present. Mg.	Apparent TiO_2 after heating. Mg.	Apparent TiO_2. Per cent.
1	20°	30°	0.625	0.625	100
2	20	40	0.625	0.625	100
3	20	50	0.625	0.625	100
4	20	60	0.625	0.625	100
5	20	80	0.625	0.625	100
6	20	90	0.625	0.625	100
7	20	100	0.625	0.425	68
8	20	110	0.625	0.250	40
9	20	120	0.625	0.150	24

Effect of Fluorine.

Inasmuch as fluorides exhibit the well known bleaching effect on the yellow color produced by the addition of hydrogen peroxide to a titanium solution, the action of hydrofluoric acid on the thymol titanium color was studied. Fluorides or hydrofluoric acid bleach the color. In this connection it should be noted that from the preliminary treatment of a titanium-bearing material in order to bring it into concentrated sulfuric acid solution, it is practically impossible for fluorides to be present.

TABLE VIII.

No.	TiO_2 present. Mg.	Fl_2 present. Mg.	Apparent TiO_2. Mg.	Apparent TiO_2. Per cent.
1	0.625	0.26	0.588	95.6
2	0.625	0.52	0.576	93.7
3	0.625	0.78	0.448	72.2
4	0.625	1.04	0.388	62.2
5	0.625	1.30	0.338	54.1
6	0.625	1.52	0.301	48.9
7	0.625	1.82	0.276	44.2
8	0.625	2.08	0.250	40.1
9	0.625	2.34	0.213	34.1
10	0.625	2.60	0.187	30.0
11	0.625	2.86	0.150	24.0

Effect of Chlorides, Phosphates, Tin and Tungsten.

Solutions of various strengths containing hydrochloric acid, phosphoric acid and tin were systematically added to a thymol sulfuric acid solution and are apparently without any effect on the coloration. Tungstic acid, on the other hand, markedly affects the color in direct ratio to the amount of tungsten present.

TABLE IX.

No.	TiO_2 present. Mg.	WO_3 present. Mg.	Apparent TiO_2. Mg.
1	2.2	0.47	2.48
2	2.2	0.94	2.75
3	2.2	1.41	3.01
4	2.2	1.88	3.25
5	2.2	2.35	3.50

Of the various organic bodies which produce distinctive colorations with titanium in concentrated sulfuric acid, thymol, phenol, hydroquinone, salicylic acid and chromotropic acid, are the most distinctive. For various reasons thymol produces the most satisfactory coloration which can be used for the detection and estimation of small amounts of titanium. The intensity of the coloration produced by thymol in sulfuric acid with titanium is at least twenty-five times as great as that produced in the hydrogen peroxide method; hence the method is applicable to smaller amounts of titanium than can be determined by the Weller method.

The method possesses certain advantages in simplicity and small number of operations. The actual time for the fusion, dilution and comparison is short. With a standard prepared the actual working time of the method is less than an hour. The only process requiring time is for the sulfuric acid to cool to room temperature and this can be facilitated by use of a constant temperature bath.

The sample of the titanium-bearing substance is usually most conveniently brought into solution by fusing with potassium acid sulfate. The fusion can be taken up in concentrated sulfuric acid and, after adding an excess of thymol in sulfuric acid, diluted to a definit volume and the color compared in a colorimeter with a standard titanium solution.

MADISON, WIS.

NORMAL AND ABNORMAL CASES OF SPECIFIC VOLUME OF BINARY LIQUID MIXTURES.

BY H. S. VAN KLOOSTER.

Received December 11, 1912.

A recent communication of Mr. A. L. Hyde,[1] concerning the specific gravity of paranitrotoluene dissolved in carbon bisulfide, led me to look for some cases of normal and abnormal specific volumes. A close inspection of the available data led me to the conclusion that the case of paranitrotoluene and carbon bisulfide cannot be qualified as an abnormal one, as was suggested by Mr. Hyde.

It is well known that the properties of aqueous solutions are highly influenced by electrolytic dissociation and probably by the formation of hydrates. To eliminate these factors in studying the properties of mixed liquids it is desirable to choose, for examination, such pairs of substances as do not show such abnormal behavior. One of the first investigators in this field of research seems to have been Guthrie,[2] who studied the volume changes and thermal effects attending mixtures of some organic liquids. He also determined the vapor pressures of binary mixtures and thereby anticipated the most valuable work of Konowalow, Young, Kuenew, Lawidsky, and others. The experiments of Lawidsky[3] form the starting point for the accurate and very interesting determinations of specific volume at different temperatures of binary organic liquids, executed by Hubbard.[4] His results are discussed in the light of Dolezalek's theory of chemical reactions between the two components.[5] The experiments were executed on substances that are not closely related to each other, such as carbon bisulfide and methylal, acetic acid and benzene,

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[1] THIS JOURNAL, 34, 1507 (1912).

[2] *Phil. Mag.*, [5] 18, 495 (1884).

[3] *Z. physik. Chem.*, 35, 129 (1900).

[4] *Ibid.*, 74, 207 (1910).

[5] *Ibid.*, 64, 727 (1908).