

enough for practical purposes and much more satisfactory on account of the simplicity of the apparatus and the fact, that, when desired, the older methods with small currents may be used with the same electrode, and without alteration of the rest of the apparatus.

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SENSITIVENESS OF THE COLORIMETRIC ESTIMATION OF TITANIUM.¹

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The color produced by hydrogen peroxide in titanium solutions serves for the estimation of small amounts of titanium and also, through a bleaching effect upon it, for small quantities of fluorine. At first thought one might suppose that there would be a concentration of maximum accuracy for this estimation, but it has been shown that there is in general a wide range of concentration over which the accuracy of a colorimetric comparison remains practically constant.² The object of the experiments here described was to establish the range of suitable concentrations in the case of titanium.

In any colorimetric comparison there is a limit to the difference of shade, or rather the difference in intensity of color, which the eye can detect. One may prepare two known solutions, one of which will be just perceptibly stronger in color, the other just perceptibly weaker than a given unknown solution. The difference in concentration of the two extremes, divided by 2, will be a certain *fraction* of the mean total substance present, and this fraction, expressed as a percentage, may be said to represent the maximum error of the comparison, or the *perceptible difference*. In comparing two solutions by a single setting, it is evident that the setting may fall anywhere between the two limits. Hence an average of several readings is essential. An equally good procedure is to determine the two limits and take the mean as the correct reading.

It was sought to determine the "perceptible differences" for various titanium solutions. The comparisons were made in the colorimeter devised by George Steiger, of the U. S. Geological Survey.³ Instead of preparing many solutions the comparisons were made by sliding one of the cells. Scale distances were taken as proportional to concentrations. One cell was set to read 10, the other was set to appear either stronger or weaker as the case might be. After alternately resting the eyes and observing the cells a number of times, when a plurality of observations indicated that there was a difference in intensity, the position was noted.

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² D. W. Horn and Sue A. Blake, *Am. Chem. J.*, **36**, 202 (1906).

³ *THIS JOURNAL*, **30**, 215 (1908).

If no difference was perceptible a new setting was made and tried in the same way. The judgment is noticeably better immediately after resting the eyes. The difference in the two final settings, one stronger, the other weaker than the reference solution, divided by 20, gives the "perceptible differences" of the comparison. Division by 2 is made because the perceptible difference was doubly determined, and by 10 because the scale readings were made in a layer of 10 cm. This percentage error or limit of perception will then apply to any given titanium determination, whatever may be the volume of the solution. The solutions contained about 3 per cent. of sulfuric acid and 2 per cent. of "dioxigen."

PEROXIDIZED TITANIUM SULFATE.					
Expt.	Concentration Mg. TiO ₂ . in 100 cc.	Color.	Reading on cell stronger than reference.	Reading on cell weaker than reference.	Perceptible difference. Per cent.
1	0.30	Very slight	8.7	11.8	15.
2	0.63	Pale straw	7.5	10.5	15.
3	1.0	Pale straw	10.0	11.1	7.5
4	1.3	Straw	9.3	12.0	14.
5	1.6	Straw	10.0	11.3	6.5
6	1.6	Straw	9.8	11.0	6.0
7	2.5	Lemon-yellow	9.2	10.7	7.5
8	4.0	Lemon-yellow	9.3	10.5	6.0
9	5.0	Yellow	9.2	10.8	8.0
10	8.4	Yellow	9.3	10.5	6.0
11	10.0	Yellow	8.8	10.3	7.5
12	11.2	Yellow	9.7	10.8	5.5
13	15.0	Yellow	9.7	10.8	5.5
14	20.0	Orange-red	9.4	10.8	7.0
15	20.0	Orange-red	9.8	10.9	5.5

Solutions stronger than the last in the table are not suitable for the estimation of titanium by colorimetry. It appears that the accuracy of the comparison is practically constant for concentration ranging from 1.5 to 20 mg. TiO₂ in 100 cc., but falls off noticeably in weaker solutions. In the latter a fair comparison can still be obtained by using a larger layer of liquid. The fraction 6.5 per cent. expresses the difference in concentration between two solutions with a just perceptible difference in intensity, as viewed in the colorimeter described. Although this percentage will vary somewhat for different observers and even for the same observer at different times, the range of suitable concentration will average about the same for the majority of persons. In any case the experiments show that the accuracy is practically constant over a wide range.

A determination of titanium by colorimetry may be made much more accurately than the above *perceptible difference*. In the first place any constant error in the colorimeter may be eliminated by the principle of comparing by substitution, that is, by substituting an unknown for a known solution in *one* of the cells, referring each to the same reference

solution in the other cell. Then one may take the mean of the extreme limits, or of a large number of settings for apparent equality. In one case the method of extreme limits gave 9.8 and 10.9, the mean being 10.35 and ten matchings gave a mean of 10.30, the extremes being 9.9 and 11.4. Determinations of five unknown solutions, comparing by substitution and making 10 settings in each comparison, gave the following results.

Taken.	Found.	Error. Per cent.
10.13	10.26	+1.3
10.46	10.52	+0.7
10.73	10.45	-2.8
10.79	10.71	-0.8
11.17	11.01	-1.6

It therefore seems safe to conclude that titanium may be determined by colorimetry to about 2 per cent. This is a very fortunate circumstance for it enables one to determine titanium quickly in mixtures containing columbium, tantalum, zirconium, tin or other elements whose chemical separation is a lengthy, if not imperfect, procedure.

It is interesting to compare the above results with those obtained by Horn and Blake with chromate and copper solutions, using Nessler tubes.¹ Some of their results are given here, in a form slightly recalculated to show the "perceptible difference" as used above.

Potassium Chromate.			
Expt.	Concentration Mg. KCr in 50 cc.	Perceptible difference in mg.	Perceptible differ- ence in per cent.
1	10.5	3.98	38.
3	3.9	0.39	10.
4	2.6	0.18	7.
5	1.3	0.07	5.
7	0.65	0.002	0.3
9	0.26	0.005	2.
11	0.16	0.011	7.
13	0.08	0.0007	0.9
15	0.017	0.008	47.

Copper Sulphate			
Expt.	Concentration Mg. Cu in 50 cc.	Perceptible difference in mg.	Perceptible differ- ence in per cent.
1	1930.	154.	8.
3	130.	12.4	10.
5	69.5	5.4	8.
7	57.2	5.8	10.
9	45.8	4.6	10.
11	37.1	3.9	11.
13	30.9	3.1	10.
15	19.3	1.2	6.3
17	9.7	1.7	18.

¹ *Loc. cit.*, pp. 196 and 200.

These investigators consider that Expt. 4 with chromium and Expt. 5 with copper fall in the range of concentration where the accuracy is constant and a maximum. The normal perceptible difference for chromium is therefore about 7 per cent. and for copper 8 per cent. This appears to be almost the same as for titanium, 6.5 per cent.

Summary.

The accuracy of the colorimetric estimation of titanium is practically constant over concentrations ranging from the strongest down to those containing about 1.5 mg. TiO_2 in 100 cc. The change in concentration required to produce a perceptible difference in intensity between two solutions, at favorable concentrations, was found to be about 6.5 per cent. which does not differ much from the results of others with chromium and copper solutions. With suitable precautions, such as comparing by substitution and taking the mean of several settings or of the two perceptibly different extremes, the accuracy of the colorimetric comparisons appears to be about 2 per cent.

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A CRUCIBLE FURNACE.

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The chief feature of this furnace consists in the replacement of the greater part of the usual solid clay or earthenware wall by an equal or greater thickness of a non-conducting refractory powder, such as light magnesia, kaolin, or even sifted ashes. As compared with a furnace having solid walls composed of clay or some similar substance, the furnace is lighter; cheaper in construction, quicker in heating, and better insulated—hence, it gives a higher temperature and is more economical as to fuel—and wear or damage of any kind is much more circumscribed and accessible and much more easily and cheaply repaired. The insulating layer can be made as thick as desired, with corresponding reduction in the leakage of heat, especially in the region of highest temperature; whereas the practicable thickness of a clay wall is sharply limited by the tendency to crack on change of temperature common to all large masses of poor heat conductors.

This furnace has so far been constructed only in the form of a small gas-fired crucible furnace, with the flame entering at the bottom. In its simplest form it can be improvised in a few minutes from the commonest and most worthless of waste materials. A large cylindrical ether or oil can serves for the outer container; a shovelful of sifted hard-coal