The Electrometric Standardizing of Titanous Solutions

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THE ELECTROMETRIC STANDARDIZING OF TITANOUS SOLUTIONS. (Preliminary Report)

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The great value of titanous salts in analytical chemistry has become well known through the work of many chemists. Titanous chloride has been used in determining not only inorganic but also many organic substances, which are likely to be colored or to give colored solution on reduction, thus interfering in the accurate determination of end-points in the usual methods of analysis where colored indicators are used. Such difficulties would, of course, be removed by the application of the voltage method. Moreover, so intensely reducing is the titanous ion that an interval of nearly one volt is given between a slight excess of titanous ion and excess of such oxidizing agents as dichromate and permanganate, when the calomel-platinum cell is used, and this wide interval permits the determination with titanium of two oxidizing agents of quite different intensities when present in the same solution.

The application of the electrometric method in determinations with titanium seemed to promise so much of value and convenience that we took up the subject early in the fall of 1921. At that date we could find no reference to any such application, but 2 months later discovered a reference to such a determination by Treadwell[1] and his collaborators. Their work seems merely incidental to research on a new cadmium reductor, and they mention it as interesting and probably capable of improvement. It seems they have not pursued this line further and it is believed that our work does not interfere with theirs, nor with that of Jones and Lee[2] on the electrometric titration of azo dyes.

We sought in the beginning to determine whether a titanous solution could be easily and accurately standardized with the standard solutions found in every laboratory, — permanganate and dichromate. Until quite recently titanous chloride, usually in hydrochloric acid solution, has been exclusively used in quantita-

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[1] Treadwell, Luethy and Rheiner, *Helv. Chim. Acta*, [4] **1921**, 551.
[2] Jones and Lee, *J. Ind. Eng. Chem.*, **14**, 46 (1922).

tive analysis. To avoid possible side reaction we, however, chose to use the sulfate in dil. sulfuric acid. Careful testing of the material bought on the market[3] showed the presence of even a trace of iron to be doubtful. The solution was kept in an atmosphere of hydrogen by means of the apparatus of Knecht and Hibbert[4] as improved by Thornton and Chapman.[5]

A standard potentiometer, a highly sensitive galvanometer and other standard apparatus were used. The end-points obtained by titrating titanous salt against either oxidizing agent were always marked by very sharp and large changes in potential.

In the experiments of Table I the procedure was as follows. Into the titration vessel containing 50 cc. about 0-1 N ferric alum

TABLE I

TITRATION OF TITANOUS SULFATE ELECTROMETRICALLY
WITH PERMANGANATE THROUGH THE MEDIUM
OF FERRIC IRON

KMnO$_4$ cc.	Ti$_2$(SO$_4$)$_3$ cc.	Ti$_2$(SO$_4$)$_3$ 0.05 N times
47.10	33.50	1.406
47.12	33.50	1.407
48.91	34.85	1.403
47.08	33.50	1.405
47.05	33.49	1.405
		Average 1.4052

made up to about 150 cc. with recently boiled dil. sulfuric acid, was passed a rapid stream of washed carbon dioxide for several minutes. The electrodes were inserted, stirring was commenced and titanous solution was rapidly added in sufficient quantity, but not enough to prevent a liberal excess of ferric iron. Permanganate was then added until the voltage rose to the indicated end-point as shown by the curve constructed from the data of a previous titration. The concentration of the permanganate was 0.05165 N.

The determinations of Table II were parallel with the determinations in Table I, except that the titanous solution was run into a measured volume of permanganate until the end-point was indicated by the voltage.

Though some chemists may regard it as not good practice to add a reducing solution to permanganate, and doubtless such a procedure is not best in some cases, particularly in that of oxalic acid,

3 From the LaMotte Chemical Company.
4 Knecht and Hibbert, "New Reduction Methods in Volumetric Analysis," Longmans, Green and Co., p. 47; 1918.
5 Thornton and Chapman, Jour. Am. Chem. Soc., 43, 91 (1921).

TABLE II

TITRATION OF TITANOUS SULFATE BY ADDITION TO
PERMANGANATE SOLUTION

$KMnO_4$ cc.	$Ti_2(SO_4)_3$ cc.	$Ti_2(SO_4)_3$ 0.05 N times
47.00	33.35	1.409
.47.08	33.48	1.406
48.91	34.83	1.404
48.86	34.80	1.404
	Average	1.4057

the results in Tables I and II are identical within the limit of ex-
perimental error. One of us[6] found that permanganate and hy-
driodic acid could be titrated by running one into the other in-
terchangeably without apparent difference.

A new solution of titanous sulfate was made up and standard-
ized with 0.05 N potassium dichromate solution which was used
in essentially the same way as the permanganate in the experi-
ments of Tables I and II. Table III contains the results of its
titration through the medium of ferric iron.

TABLE III

ELECTROMETRIC TITRATION OF TITANOUS SULFATE WITH
DICHROMATE THROUGH THE MEDIUM OF FERRIC IRON

$K_2Cr_2O_7$ cc.	$Ti_2(SO_4)_3$ cc.	$Ti_2(SO_4)_3$ 0.05 N times
29.28	30.40	0.9631
29.00	30.07	0.9644
29.80	30.90	0.9644
31.15	32.30	0.9644
	Average	0.9641

The results of the direct titration of titanous salt by adding it
to dichromate to the end-point are shown in Table IV.

TABLE IV

ELECTROMETRIC TITRATION OF TITANOUS SULFATE BY
ADDING IT TO POTASSIUM DICHROMATE

$K_2Cr_2O_7$ cc.	$Ti_2(SO_4)_3$ cc.	$Ti_2(SO_4)_3$ 0.05 N times
25.00	25.98	0.9623
27.83	28.95	0.9613
30.35	31.51	0.9632
30.57	31.68	0.9649
	Average	0.96292

In order to determine the extent to which the standardizations
with permanganate and dichromate agree and confirm each other,

[6] Hendrixson, Jour. Am. Chem. Soc., 43, 1309 (1921).

the new solution of titanous sulfate was also treated with the same solution of permanganate used in Tables I and II, running the titanium solution into the permanganate. The results are seen in Table V.

TABLE V
DIRECT ELECTROMETRIC TITRATION OF NEW TITANOUS SULFATE SOLUTION WITH PERMANGANATE

KMnO$_4$ cc.	Ti$_2$(SO$_4$)$_3$ cc.	Ti$_2$(SO$_4$)$_3$ 0.05 N times
42.46	43.90	0.9672
37.20	38.75	0.9600
36.09	37.55	0.9611
49.25	50.94	0.9668
31.37	32.62	0.9617
		Average 0.96336

The average result with permanganate is, doubtless largely by accident, almost precisely the same as the averages obtained with dichromate, and the fact makes it extremely probable that both methods are accurate. Any question in this respect is settled by the work of Jatar[7] which proved that dichromate and titanous chloride act upon each other quantitatively, the valence of chromium changing from 6 to 3 and that of titanium from 3 to 4; in fact, he used titanous chloride for standardizing dichromate and employed a mixture of ferrous iron and thiocyanate as external indicator. It would seem that either oxidant may confidently be used either directly or through the medium of ferric iron for the determination of titanium by the electrometric method.

The sharp change in potential from a slight excess of titanous ion to slight excess of permanganate is about 0.9 volt, and from a slight excess of titanous ion to an excess of dichromate ion about 0.6 volt, and as already indicated these facts may permit the determination in certain instances of 2 substances of quite different oxidizing or reducing power when present in the same solution; for example, titanous and ferrous ions with permanganate or dichromate, ferric ion and permanganate with titanous ion. We have made such titrations of mixtures, and that they are entirely practicable is best shown by the voltage curves in Fig. 1. Curve 1 shows the titration of a mixture of ferrous and titanous ion with permanganate; Curve 2 shows the titration of ferrous and titanous ions with dichromate; Curve 3 is the reverse of Curve 1 and shows the titration of ferric ion and permanganate with titanous ion; Curve 4 is the reverse of 2 and illustrates voltage changes in titrating dichromate and ferric iron with titanous ion.

7 Jatar, J. Soc. Chem. Ind. 27, 673 (1908).

SUMMARY

This paper emphasizes the value of titanous ion in volumetric analysis, the advantages of the electrometric method for end-points in its use, and shows that titanous sulfate solutions may be easily and accurately standardized with permanganate or dichromate, either directly or through the medium of a ferric-iron solution.
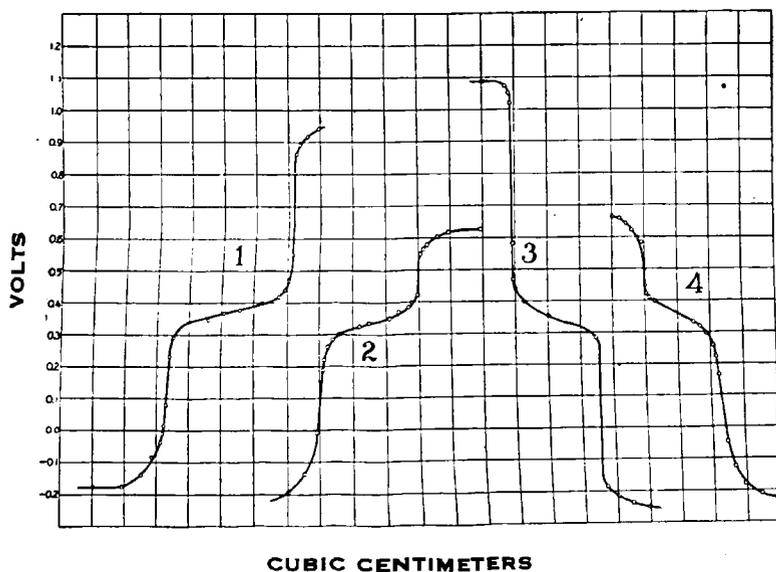
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CUBIC CENTIMETERS

FIGURE 1