

glass Siemens ozonizer tube, furnished by a high voltage induction coil. The other was an arc from a 20,000-volt Thordarson wireless transformer passing through chlorine at a pressure of 6 cm. of mercury. Since metallic electrodes are attacked by chlorine, glass-covered mercury electrodes were used in this work. Two 5mm. glass tubes were sealed into the ends of a 20mm. glass tube in such a way as to project into it and leave a gap between them for the arc about 8 cm. in length. The inner ends of the tubes were sealed smoothly round, and the tubes were then filled with mercury, thus forming glass-covered mercury electrodes projecting into the tube. In no case was any acid formed.

There being no evidence for the existence of an active form of chlorine, the explanation of Draper's experiment will be found in that of the induction period itself. The absence of the active chlorine, therefore, makes more attractive recent experiments<sup>9</sup> on the possibility that the latent period is caused by an inhibition, the removal of which is the first action of the light.

### Summary

Neither a 3000-watt Bovie mercury arc lamp nor a high potential electric discharge was found to be capable of imparting to chlorine an activity such that it will react with hydrogen in the dark. Draper's experiment, however, was confirmed. The fact that the latent period in the hydrogen-chlorine reaction can be destroyed by previous insolation of the chlorine must be attributed to the destruction of inhibiting impurities rather than to any activation of the chlorine itself.

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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 not only in determining inorganic but also many organic substances, which are likely to be colored or to give colored solutions 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 deter-

mination 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<sup>1</sup> 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<sup>2</sup> 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 quantitative analysis. To avoid possible side reactions we, however, chose to use the sulfate in dil. sulfuric acid. Careful testing of the material bought on the market<sup>3</sup> 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<sup>4</sup> as improved by Thornton and Chapman.<sup>5</sup>

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 made up to about

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

KMnO <sub>4</sub> Cc.	Ti <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> Cc.	Ti <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> 0.05 <i>N</i> 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

Av. 1.4052

<sup>1</sup> Treadwell, Luethy and Rheiner, *Helv. Chim. Acta*, [4] 1921, 551.

<sup>2</sup> Jones and Lee, *J. Ind. Eng. Chem.*, 14, 46 (1922).

<sup>3</sup> From the LaMotte Chemical Company.

<sup>4</sup> Knecht and Hibbert, "New Reduction Methods in Volumetric Analysis," Longmans, Green and Co., 1918, p. 47.

<sup>5</sup> Thornton and Chapman, *THIS JOURNAL*, 43, 91 (1921).

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.

TABLE II

TITRATION OF TITANOUS SULFATE BY ADDITION TO PERMANGANATE SOLUTION

KMnO <sub>4</sub>	Ti <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	Ti <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>
Cc.	Cc.	0.05 <i>N</i> 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

Av. 1.4057

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, the results in Tables I and II are identical within the limit of experimental error. One of us<sup>6</sup> found that permanganate and hydriodic acid could be titrated by running one into the other interchangeably without apparent difference.

A new solution of titanous sulfate was made up and standardized with a 0.05 *N* potassium dichromate solution which was used in essentially the same way as the permanganate in the experiments 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 ALUM

K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	Ti <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	Ti <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>
Cc.	Cc.	0.05 <i>N</i> 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

Av. 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.

<sup>6</sup> Hendrixson, THIS JOURNAL, 43, 1309 (1921).

TABLE IV  
ELECTROMETRIC TITRATION OF TITANOUS SULFATE BY ADDING IT TO POTASSIUM

K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> Cc.	DICHROMATE	Ti <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> 0.05 N times
	Ti <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> Cc.	
25.00	25.98	0.9623
27.83	28.95	0.9613
30.35	31.51	0.9632
30.57	31.68	0.9649

Av. 0.96292

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

K <sub>2</sub> MnO <sub>4</sub> Cc.	Ti <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	Ti <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> 0.05 N times
	Cc.	
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

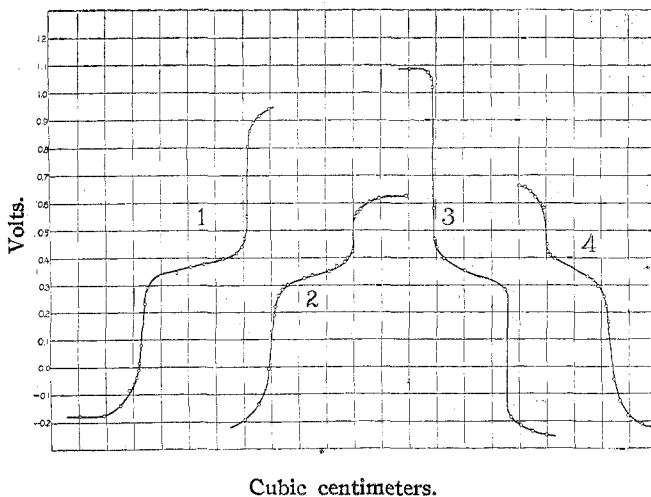
Av. 0.96336

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<sup>7</sup> 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 a 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

<sup>7</sup> Jatar, *J. Soc. Chem. Ind.*, **27**, 673 (1908).

dichromate, ferric ion and permanganate or dichromate 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.

### 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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