This gives a means of determining molybdenum in alkali molybdates accurate to within 0.5 mg. and, indirectly, phosphorus in the precipitate of ammonium phosphomolybdate. Tungstic acid presents no interference and it also eliminates the necessity of applying a correction for the excess titanous solution required to give the end-point.

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THE ELECTROMETRIC TITRATION OF SELENIUM IN THE PRESENCE OF TELLURIUM, IRON AND COPPER

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Received December 8, 1922

Introduction

The reduction of selenious acid to metal by titanous chloride was observed by Moser[1] and also by Monnier.[2] Moser attempted to develop a volumetric method for selenium based on this reaction using methylene blue as indicator but the results obtained were invariably too high. This was due to the further reduction of the selenium to hydrogen selenide, a compound which had been shown to exist under similar conditions by Pleischl[3] and Trautmann.[4]

Under the condition imposed by Moser, namely, a hot hydrochloric acid solution, the electrometric end-point is either absent or very poor, but in a cold solution containing 25 to 75% of conc. hydrochloric acid and saturated, or nearly so, with sodium chloride, the end-point with the previously described polarized bimetallic electrode system[5] with platinum electrodes is excellent. The presence of the sodium chloride is important. It insures rapid and uniform coagulation of the selenium hydrosol and increases the sharpness of the change in voltage at the end-point. The use of a cold solution also eliminates the almost inevitable loss of selenium by volatilization.

The character of the end-point for this titration is somewhat difficult to describe but is readily discovered by experiment. After enough of the titrating solution has been added to give a constant potential, there is little change until within a short distance of the end-point. Slight fluctuations in the e.m.f. may be manifested; the resistance of the solution is so low that the galvanometer is extremely sensitive. The characteristic rise occurs, with the fall immediately following. The condition of the solution with respect to acidity and foreign salts determines which of the two pre-

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[1] Moser, *Z. anal. Chem.*, **57,** 277 (1918).

[2] Monnier, *Ann. chim. anal. appl.*, **20,** 1 (1915).

[3] Pleischl, *Kastner Arch.*, **93,** 430.

[4] Trautmann, *Bull. soc. ind. Mülhouse,* **61,** 87(1891).

[5] Willard and Fenwick, This Journal, **44,** 2516 (1922).

dominates. Increasing the polarizing e.m.f. from 0.1 to 1.0 volt makes no appreciable difference in the character of the end-point.

As is the case with other titanous titrations the actual voltage change may not be large, in fact may not amount to more than a few millivolts. The galvanometer should be sufficiently sensitive to give a distinct deflection for a change in potential of 1 mv. between the electrodes.

It is inadvisable to clean the electrodes between titrations more than to wash them with distilled water. The small amount of selenium adhering after the first titration increases the sharpness of the end-point. The coagulation of the colloidal selenium in the near vicinity of the end-point is quite distinct and affords a fairly close visual check on the titration.

Titration of Selenious Acid with Titanous Sulfate

A pure commercial selenium was dissolved in nitric acid, evaporated to dryness, and the selenium dioxide obtained purified by two sublimations. An approximately 0.05 *N* aqueous solution of selenious acid was prepared and standardized gravimetrically by reduction with hydrazine sulfate according to the method of Gutbier, Metzner and Lohmann.[6] In four experiments the weights of selenium obtained from 100.00 cc. of the solution were 0.0994, 0.0995, 0.0997, 0.0996 g., or an average of 0.0995 g. The solution was, therefore, 0.0503 *N*. The purity of the selenium dioxide was 99.1%, the rest being, doubtless, moisture.

Table I

Titration of Selenious Acid with Titanous Sulfate

Total initial volume in all cases, 100 cc.

SeO_2 taken Cc.	$Ti_2(SO_4)_3$ required Cc.	Av. Cc.	$Ti_2(SO_4)_3$ calc. from Fe factor Cc.	$Ti_2(SO_4)_3$ calc. from $KMnO_4$ factor Cc.
10.00	6.85			
10.00	6.75	6.80	6.70	6.72
15.00	10.15			
15.00	10.17			
15.00	10.18	10.15	10.05	10.08
15.00	10.10			
20.00	13.52			
20.00	13.52	13.52	13.40	13.44
30.00	20.15			
30.00	20.26			
30.00	20.15	20.19	20.10	20.16
30.00	20.20			
40.00	26.80			
40.00	26.80	26.80	26.80	26.88

Samples of this solution were titrated electrometrically with titanous sulfate[7] in solutions containing 40% of conc. hydrochloric acid and sat-

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[6] Gutbier, Metzner and Lohmann, *Z. anorg. Chem.*, **41**, 297 (1904).

[7] Prepared by the electrolytic reduction of titanic sulfate and stored in an atmosphere of hydrogen. Thornton and Chapman, This Journal, **43**, 91 (1921).

urated with sodium chloride. All titrations were conducted in a current of carbon dioxide.[8] The titanium solution was standardized against a solution of ferric sulfate,[9] prepared from electrolytic iron of known purity, and against potassium permanganate.[10] Against the former it was found to be 0.0750 *N*, against the latter, 0.0748 *N*.

From a comparison of the volumes of titanous sulfate used in the several determinations it is evident that the excess of the titrating solution required to give the end-point reaction was very close to 0.10 cc. (The titrations

TABLE II

EFFECT OF HYDROCHLORIC ACID

Total initial volume in all cases, 100 cc.

SeO_2 taken Cc.	$Ti_2(SO_4)_3$ required Cc.	Vol. of HCl (Sp. gr. 1.18) in 100 cc. of soln. Cc.	Character of end-point
15.00	11.44	75	Very good. Fall at end-point not permanent but definite
15.00	11.40	50	Rise and fall extremely sharp
15.00	11.42	35	Very good
30.00	22.77	35	Very good
15.00	11.43	25	Rise more marked than fall
30.00	22.70	25	Good
20.00	15.08	25	Good
10.00	7.53	25	Good
15.00	...	10	Poor

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[8] A convenient arrangement for titrating in an atmosphere of carbon dioxide is shown in the sketch.

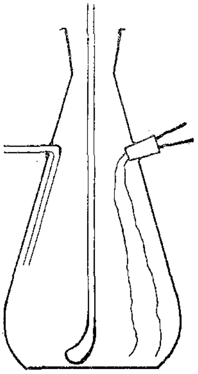

Fig. 1.

The platinum electrodes are slipped through a small 2-hole rubber stopper and inserted into a hole made about 1/3 the distance down from the mouth of a 500cc. Erlenmeyer flask equipped with a gas inlet. The inlet tube must not dip below the surface of the solution.

[9] Titrated to the disappearance of the color of ferric thiocyanate. Thornton and Chapman, Ref. 7.

[10] Titrated by adding it to the permanganate in sulfuric acid solution. The permanganate was standardized against sodium oxalate from the Bureau of Standards.

with the 40.00cc. samples were evidently a little low.) When this correction is made, the check with the amount of titanium calculated from the iron factor is usually within 0.02 cc. The titration of the selenious acid proceeds, then, according to the equation: $SeO_2 + 4HCl + 4TiCl_3 = Se + 4TiCl_4 + 2H_2O$. There can be, therefore, no secondary reaction such as found by Moser[1] and no empirical standards are necessary in the determination.

Effect of Varying the Concentration of Hydrochloric Acid

The effect of varying the hydrochloric acid concentration is shown in Table II.

An acidity of 25 to 75 cc. of conc. hydrochloric acid in 100 cc. of solution is entirely satisfactory.

Effect of Sulfuric Acid

In the preparation of an actual sample of metallic selenium for analysis it is very desirable to avoid the use of hydrochloric acid for removing the nitric acid in which the material is dissolved. In hydrochloric acid solution selenium chloride is appreciably volatile at the boiling point. For this reason the effect of sulfuric acid upon the titration was studied.

TABLE III

EFFECT OF SULFURIC ACID

15.00 cc. of 0.05 *N* selenious acid solution was used in each titration. The solutions were saturated with sodium chloride and had an initial volume of 100 cc.

$Ti_2(SO_4)_3$ Cc.	Vol. of conc. acid[a] in 100 cc. of soln. Cc.	Character of end-point
11.37	50 HCl	(Control titration)
11.40	50 HCl + 5 H_2SO_4	Rise long and marked, fall slow. Titrated to end of rise
11.40	50 HCl + 10 H_2SO_4	Not quite as good as the preceding. No permanent fall. Not difficult to determine end-point

[a] Refers to HCl, d. 1.18, or to H_2SO_4, d. 1.84.

The acid may be present in amounts up to 5 or 10 cc. per 100 cc. of solution but is to be avoided in any considerable quantity.

The non-volatility of selenium in hot sulfuric acid was shown by the evaporation of samples of the selenium solution with 5 cc. of conc. sulfuric acid until dense fumes formed and then titration after the addition of sodium chloride and hydrochloric acid. The maximum variation was 0.06 mg. in a total of 15 mg., or 0.4%. The end-point, however, was not quite as sharp as when the fuming had been omitted.

Effect of Tellurium

Of the common associates of selenium, tellurium is probably of the greatest interest in its effect upon the titration of the former element. In a hot hydrochloric acid solution of moderate concentration tellurium is rapidly reduced by titanous salts, but in the cold the reduction, if any takes place, is very slow.

Metallic tellurium was carefully freed from selenium by Keller's method,[11] reprecipitated as metal, again dissolved in nitric acid, evaporated to fumes of sulfuric acid and dissolved in hydrochloric acid. Various amounts of this solution were added to known amounts of selenious acid solution and determinations made as outlined in Table IV.

TABLE IV

EFFECT OF TELLURIUM

15.00 cc. of 0.05 N selenious acid was used in each titration. Total initial volume, 100 cc.

Ratio, wt. Te:wt. Se	$Ti_2(SO_4)_3$ Cc.	Vol. of HCl (Sp. gr. 1.18) in 100 cc. of soln.	Character of end-point
...	11.34	50	(Control titration)
4:5	11.33	50	Sharp rise, no fall with excess
4:5	11.35	50	Regular fall with excess
8:3	11.35	50	Distinct rise, no fall with excess
4:1	11.35	50	No fall with excess
8:1	11.35	50	No fall
8:1	11.30	25	A fall
8:1	11.35	25	A fall
8:1	11.35	25	No fall. End-point a change in rate of rise

Tellurium even in large amounts does not interfere in the titration of selenium but it seems to affect the character of the end-point much as does sulfuric acid. The fall in potential as the end-point is passed does not always occur, but the rise is fully as sharp as in the absence of these substances. There is no difficulty in recognizing the completion of the reaction.

Effect of Iron

One of the most surprising and interesting things in connection with the selenium determination is the fact that the volume of titanium solution used in titrating mixtures of selenium and ferric iron is identical with that for the selenium alone although ferrous iron is formed during the precipitation. The character of the end-point is much the same as that described later with mixtures of selenium and copper, but no second end-point is obtainable at the point of complete reduction of both elements.

In Table V the solutions contained 30.00 cc. of conc. hydrochloric acid in a volume of 100 cc. and were saturated with sodium chloride.

The behavior of selenium under these conditions seemed at first paradoxical. It was observed, however, that with large amounts of iron the precipitation was apparently incomplete. From two samples, one of which contained twice as much ferric iron as the other, the selenium was filtered

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[11] Keller, THIS JOURNAL, **19,** 771 (1897). Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Company, 3rd ed., **1922,** p. 423.

at the end of the titration, thiocyanate was added, and more of the titanous solution run in. No sharp color change occurred. The deep red faded slowly only to reappear in a few seconds. The amount of titanium required for an approximate end-point was twice as much in the solution containing double the amount of iron. After much more titanous sulfate had been added there was a further precipitation of selenium. It appeared that ferric iron and selenious acid might form a rather unstable compound in which the selenium is reduced only with difficulty, requiring a large excess of titanium. An amount of ferric iron equivalent to the combined selenium is reduced along with the free selenious acid and the numerical result of the titration, therefore, is unaffected. In the second series the amount of iron was increased until no precipitation occurred, without affecting the results, thus supporting this view. The exact composition of the compound was not investigated.

TABLE V

EFFECT OF IRON

SeO_2 taken Cc.	0.05 *N* Fe^{+++} added Cc.	Ti^{+++} req. Cc.	Remarks
15.00	..	10.60	
15.00	1	10.58	
15.00	5	10.52	
15.00	10	10.61	
30.00	1	21.25	
30.00	10	21.26	
		SECOND SERIES	
15.00	..	10.15	
15.00	25	10.22	Pptn. very incomplete
15.00	35	10.17	Pptn. very incomplete
15.00	50	10.15	Pptn. slight
30.00	50	20.20	Pptn. greater than preceding
10.00	75	6.82	No pptn. End-point a little slow

Effect of Copper

In hydrochloric acid solution trivalent titanium reduces cupric salts to the cuprous form.[12] When present with selenium, however, the latter is reduced first and apparently selectively. The electrometric titration gives two end-points, one when the selenium is entirely precipitated and a second at the completion of the reduction of the copper. Toward the end of the first reaction the voltage starts to rise slightly. There is then a long, distinct, upward swing that marks the end-point, followed usually by

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[12] Rhead, *J. Chem. Soc.*, **89,** 1491 (1906). Knecht and Hibbert, "New Reduction Methods in Volumetric Analysis," Longmans, Green and Co., **1918.** Moser, *Chem.-Ztg.*, **34,** 1126 (1912). Monnier, *Ann. chim. anal.*, **21,** 109 (1916). Mach and Lederle, *Landw. Vers. Sta.*, **90,** 191 (1917). Thornton, THIS JOURNAL, **44,** 998 (1922).

continued rise. The copper end-point is a second sharp rise.[13] It is not quite as clear as the first but readily distinguishable after a little experience.

Table VI records a number of titrations carried out in the presence of copper.

Table VI

Effect of Copper

All solutions titrated had an initial volume of 100 cc., contained 30–40% of conc. hydrochloric acid and were saturated with sodium chloride.

SeO_2 taken Cc.	0.05 *N* $CuSO_4$ added Cc.	Ti^{+++} req. for Se end-point Cc.	Total Ti^{+++} used Cc.	Ti^{+++} req. for Cu Cc.
...	5.00	...	...	3.55
15.00	..	10.50	...	..
15.00	..	10.50	...	..
15.00	5.00	10.53	14.02	3.49
15.00	10.00	10.50	17.60	7.10
15.00	1.00	10.52	...	..
		Second Series		
15.00	..	10.65	...	..
15.00	5.00	10.65	...	..
30.00	5.00	21.24	...	..

Summary

1. The volumetric reduction of selenious acid to selenium by titanous sulfate is rapid and accurate to within 0.1 mg. in cold hydrochloric acid solution saturated with sodium chloride.
2. Under these conditions tellurium is not reduced and its only effect is to modify the nature of the end-point.
3. Moderate amounts of sulfuric acid have no deleterious effect upon the determination of the end-point and there is no volatilization of selenium at the fuming temperature in this acid.
4. The titration of selenium is quantitatively independent of the concentration of iron, although ferrous iron is formed in the reaction.
5. The reducing effect of trivalent titanium upon mixtures containing copper and selenium is selective, the latter being reduced first, and both elements may be determined in a single titration.

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[13] It is obvious that the method may be adapted to the determination of copper alone. A number of very accurate titrations were made in this way but this application is not stressed because of the rather large amount of other work on this reaction already published.