Oxidimetric and Reductometric Titrations in Neutral Solutions. (Application of Sodium Triphosphate as Masking Agent to Volumetric Analysis.)

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(Received December 12, 1956)

In the estimation of metallic ions in neutral media by means of oxidimetric or reductometric titrations, most of them produce insoluble hydroxides or carbonates. In the case of iron (II), its hydroxide is oxidized by the air. So the determination is incomplete. The same is the case with titanium (III). With a view to avoid these effects, the present authors have been trying to apply masking reactions to such cases. In the present paper, they show the use of polyphosphates as the masking agent and as complexing agent, and the extention of the new method will be described. The stability of the reducing standard solutions is also studied.

Oxidimetric Titration

Reagent.—The same oxidizing standard solutions given below were used as in the case of acidic media: one tenth normal solution of ceric sulfate, sodium vanadate, potassium-dichromate, -bromate, -permanganate and -triiodide. Two tenth % solutions of redox indicators were used, namely amarance for bromometry, cacoterin for chromometry, and crystal violet for permanganimetry. Sodium bicarbonate was used for neutralization and sodium triphosphate for masking.

Materials. — One tenth N solutions of iron (II)-, titanium(III)- and chromium(II)- sulfate, sodium -vanadate and -molybdate, thallium(I) nitrate, tin(II)- and antimony(III)- chloride, sodium arsenite and selenium dioxide were prepared (if necessary in an acid medium) and standardized by the usual methods.

Procedure.—Take an aliquot sample solution, add 3 g. of solid sodium triphosphate hexahydrate, stir gently, and add solid sodium bicarbonate in small portions until some pieces remain undissolved. Add a few drops of indicator and titrate with the standard solution. The solution should be moderately and constantly stirred in the course of titration. When too much triphosphate is added, a precipitate may appear. If necessary, add more sodium bicarbonate to keep the solution neutral.

Result and Discussion

(*A*) *Permanganimetry.* (Fe^{2+}, Ti^{3+}, VO^{2+}, Cr^{2+}, Mo^{5+}, Tl^{+}.) : As the masking force of triphosphate for manganese chloride is incomplete, chlorides should not be present in the sample. In the titration of iron (II), it is completely masked with triphosphate in a neutral medium and the results are satisfactory (Table I). When a fairly large amont of titanium(III) is titrated, a gelatinous substance is precipitated. The end point is given by the color change from gray to pink. Vanadium(IV) prepared by means of liquid amalgam method, is yellowish green in a neutral solution, and the end point is given by the pink color of permanganate. Chromium(II) is also green in a neutral solution, and it is not difficult to find the end point in permanganimetry. Molybdenum(V) has a pale brown color in a solution containing triphosphate; no precipitate is perceived in solutions of quinquevalent as well as hexavalent molybdenum on addition of triphosphate. Thallium(I) is oxidized to thallium(III), which gives no precipitate (Table I).

TABLE I
PERMANGANATE METHOD

Element	Sample formula	Element mg.	
		Content	Found
Fe	$FeSO_4$	54.6 163.8	54.5 163.5
Cr	$CrSO_4$	42.4 127.4	42.3 127.4
Mo	$Mo_2(SO_4)_5$	55.4 166.2	55.4 166.7
Ti	$Ti_2(SO_4)_3$	52.1 156.3	52.6 154.9
Tl	Tl_2SO_4	50.2 150.6	50.1 149.6
V	$VO(SO_4)$	36.7 110.1	36.3 109.4

(*B*) *Bromometry* (Sn^{2+}, Fe^{2+}, Ti^{3+}, As^{3+}, Sb^{3+}, Se^{4+}.): As methyl orange has a yellow color itself in a neutral medium, it is difficult to determine the end point by its decoloration. Amarans is a good redox indicator in a neutral solution which has a red color and is decomposed by oxidizing agents after the element to be oxidised has been quantitatively oxidized. Tin(II) and others are thus completely estimated bromometrically (Table II). The blank for 2 drops of the 0.2% indicator solution is about 0.01 ml. of each 0.1 N oxidizing standard solution.

TABLE II

SODIUM HYPOBROMITE METHOD

Element	Sample formula	Element mg.	
		Content	Found
As	Na_3AsO_3	34.6 103.8	34.7 104.1
Fe	$FeSO_4$	30.9 92.7	31.1 92.5
Sb	$SbCl_3$	41.1 123.3	41.2 123.5
Se	SeO_2	33.8 101.4	33.9 102.0
Sn	$SnCl_2$	35.2 105.6	35.2 104.9
Ti	$Ti_2(SO_4)_3$	43.2 129.6	43.0 128.6

(*C*) *Chromometry* (Fe^{2+}, Ti^{3+}, Sn^{2+}, Sb^{3+}.): The leuco compound is formed when methylene blue is added to iron(II) sample solution; at the end point, the former is oxidizied to the colored state. In the case of titanium(III) or tin(II), cacoterin is added which combines with these metals forming colored compounds that are decomposed and decolored at the end point. In the estimation of antimony(III), the end point is determined when the yellow color of chromate is perceived in the green color of the solution (Table III).

TABLE III

POTASSIUM DICHROMATE METHOD

Element	Sample formula	Element mg.	
		Content	Found
Fe	$FeSO_4$	45.3 135.9	45.2 136.4
Sb	$SbCl_3$	37.6 112.8	37.2 111.4
Sn	$SnCl_2$	30.9 92.7	29.9 91.5
Ti	$Ti_2(SO_4)_3$	43.2 129.6	43.6 127.8

(*D*) *Vanadometry* (Fe^{2+}, Ti^{3+}, Sn^{2+}, Sb^{3+}): The metal ions are estimated using methylene blue for iron(II), titanium(III) and molybdenum(V), and cacoterin for tin(II) (Table IV).

In the above-mentioned oxidation titrations, the effect of the following elements was studied:

Li, Na, Ca, K, Sr, Ba, Mg, Cu, Zn, Cd, B, Al, Pb, Nb, As, Mn, Sb, Cr, Ni, Co, Bi, F, Si, Zr, Th, Ce, Tl, Be, W, Ag, Hf, U, Mo, Sn, Fe, Pt, Os, Rh, Pd, and Au.

TABLE IV

SODIUM VANADATE METHOD

Element	Sample formula	Element mg.	
		Content	Found
Fe	$FeSO_4$	45.2 136.5	44.8 135.1
Mo	$Mo_2(SO_4)_5$	55.4 166.2	55.0 165.4
Sn	$SnCl_2$	30.9 92.7	29.9 91.3
Ti	$Ti_2(SO_4)_3$	37.6 112.8	37.1 110.9

Of these, Ag, Au, Hg, Cu, Sn, Sb, As, and Pd interfere with the determination of iron(II) and titanium(III), Ag, Sn, Sb, Pd and U with that of arsenic(III), and Ag, Hg, Au, Sn, As, Pd and Mo with that of antimony(III).

(*E*) *Mixture of iron(II) and titanium (III):* Total concentration of these metals is estimated by direct titration with permanganate solution (Second column in Table V). On the other hand, titanium (III) can be masked with ammonium bifluoride in the permanganate method; iron(II) can thereby be estimated after its addition, methylene blue being used as indicator (First and fourth column in Table V). Titanium(III) is estimated from the difference between these two titres (First and second column).

(*F*) *Mixture of iron(II) and vanadium (IV):* Total concentration can be determined by direct titration with permanganate solution without indicator. As the leuco compound of methylene blue is oxidized before vanadyl ion is oxidised, iron (II) can be estimated. From the difference between these two titres, vanadium(IV) can be estimated (Table VI).

(*G*) *Mixture of titanium(III) and vanadium(IV):* Total concentration can be determined by direct titration with permanganate solution without indicator, and titanium(III) can be estimated by the use of methylene blue (Table VII).

TABLE V

MIXTURE OF IRON(II) AND TITANIUM(III)

0.1229 N $KMnO_4$ used ml.		Fe mg.		Ti mg.	
NH_4HF_2 & $Na_5P_3O_{10}$ as masking agent & methylene blue as indicator	$Na_5P_3O_{10}$ as masking agent without indicator	Content	Found	Content	Found
3.78	8.08	26.2	25.9	25.6	25.4
3.78	16.64	26.2	25.9	76.1	75.7
7.59	20.46	52.3	52.1	76.1	74.8
11.38	15.66	78.5	78.1	25.4	25.2
11.35	19.97	78.5	77.9	50.7	50.6

TABLE VI

MIXTURE OF IRON(II) AND VANADIUM(IV)

0.1229 N $KMnO_4$ used ml.		Fe mg.		V mg.	
$Na_5P_3O_{10}$ as masking agent & methylene blue as indicator	$Na_5P_3O_{10}$ only	Content	Found	Content	Found
3.77	6.94	25.8	25.8	19.9	19.9
3.75	13.24	25.8	25.7	59.5	59.3
7.49	16.98	51.7	51.4	59.5	59.5
11.27	14.42	77.5	77.4	19.9	19.6
11.24	17.56	77.5	77.3	39.7	39.6

TABLE VII

MIXTURE OF TITANIUM(III) AND VANADIUM(IV)

0.1229 N $KMnO_4$ used ml.		Ti mg.		V mg.	
$Na_5P_3O_{10}$ as masking agent & methylene blue as indicator	$Na_5P_3O_{10}$ only	Content	Found	Content	Found
4.61	7.83	27.0	27.0	20.2	20.1
4.57	14.18	27.0	27.0	60.5	60.2
9.16	18.75	53.9	53.9	60.5	60.1
13.73	17.07	80.9	80.8	20.2	20.1
13.71	20.22	80.9	80.7	40.3	40.1

TABLE VIII

MIXTURE OF CHROMIUM(II) AND TITANIUM(III)

0.0898 N $KMnO_4$ used ml.		Cr mg.		Ti mg.	
NH_4HF_2 & $Na_5P_3O_{10}$ as masking agent & methylene blue as indicator	$Na_5P_3O_{10}$ only	Content	Found	Content	Found
2.71	8.89	12.7	12.6	26.6	26.6
2.69	21.22	12.7	12.6	79.8	79.6
5.41	23.93	25.4	25.3	78.9	79.8
8.12	14.24	38.1	37.9	26.6	26.3
8.11	20.49	38.1	37.9	53.2	53.1

(H) Mixture of chromium(II) and titanium(III): Total concentration is estimated by direct titration with permanganate solution without indicator; after masking titanium(III) with ammonium bifluoride, chromium(II) is determined similarly. Titanium(III) can be estimated from the difference between these titres (Table VIII).

(I) Mixture of iron(II), titanium(III) and vanadium(IV): Total concentration can be determined by means of direct titration with permanganate solution without indicator (Third column in Table IX). The sum of the concentrations of iron(II) and titanium(III) can be determined by direct titration in the presence of methylene blue (Second column in Table IX).

TABLE IX

MIXTURE OF IRON(II), TITANIUM(III) AND VANADIUM(IV)

0.0998 N $KMnO_4$ used ml.			Fe mg.		Ti mg.		V mg.	
NH_4HF_2 & $Na_5P_3O_{10}$ as masking agents & methylene blue as indicator	$Na_5P_3O_{10}$ only as masking agent & methylene blue as indicator	$Na_5P_3O_{10}$ without indicator	Content	Found	Content	Found	Content	Found
5.09	11.28	15.59	25.7	25.5	26.7	26.6	20.1	20.1
10.21	28.78	33.01	51.3	51.2	80.0	78.9	20·1	19.8
15.38	21.56	25.79	77.0	77.1	26.7	26.5	20.1	19.8
15.35	27.74	40.42	77.0	76.9	53.3	53.3	60.4	59.2
15.36	33.88	38.12	77.0	77.0	80.0	79.6	20.1	18.9
5.09	23.76	36.52	25.7	25.5	80.0	79.8	60.4	59.7

Iron(II) is estimated by means of masking titration, in the presence of ammonium bifluoride and methylene blue (First column in Table IX). From these three titrations, titanium(III) and vanadium(IV) are estimated.

Reductometric Titration

Reagent.—Add 20 g. of sodium triphosphate to one liter of 0.1 N acidic standard solution, cautiously neutralized with solid sodium bicarbonate until no more carbone dioxide is evolved. Stock the solution in a dark box. Iron(II)-, titanium (III)-, vanadium(IV)-, and chromium(II)- triphosphate solution are fairly stable. Indigo carmine, methylene blue, methyl violet, crystal violet, and amarance are used as indicators.

Material.—As the sample, solution of potassium -permanganate, -bichromate, cerium(IV)-, and iron(III)- sulfate were used, their titres being determined beforehand in acidic solutions.

Procedure.—Add 3 g. of sodium triphosphate hexahydrate to an aliquot sample solution, and neutralize it with sodium bicarbonate, avoiding an excess. Titrate the mixture with a standard solution.

Result and Discussion

(*J*) *Ferrousmetry* (MnO_4^-, IO_4^-, Ce^{4+}, CrO_4^{2-}, VO_3^-, BrO^-, Br_2, H_2O_2). Potassium -permanganate and -iodate are titrated with a reducing standard solution directly: the color of the sample solution disappears at the end point. In the cases of cerium(IV) sulfate, potassium chromate, sodium vanadate and hydrogen peroxide, cacoterin is used as indicator which imparts a violet coloration to the medium containing an excess of iron(III) solution. In the determination of hypobromite (or bromine), the indicator is decomposed before the end point, so that it is necessary to reduce BrO^- with an excess of iron(II) solution (Table X).

(*K*) *Chromometry* (IO_3^-, I_3^-, MnO_4^-, CrO_4^{2-}, VO_3^-, Ce^{4+}, Fe^{3+}, BrO^-). The solution of potassium triiodide is decolorized at the end point. In the cases of potassium -permanganate and -chromate, sodium vanadate and cerium(IV) sulfate, indigocarmine is used; neutral red may be used for chromate and neutral red as well as crystal violet for iron(III). Hypobromite is determined by back titration as in ferrousmetry (Table XI).

TABLE X

FERROUSMETRY

Element	Sample formula	Element mg.	
		Content	Found
Br	NaBrO	40.7 125.8	40.6 125.7
Ce	$Ce(SO_4)_2$	56.2 170.8	56.0 170.6
Cr	K_2CrO_4	29.3 87.7	29.2 87.6
H_2O_2		22.9 68.2	22.8 68.2
I_2	KI_3	67.8 202.4	67.5 201.6
Mn	$KMnO_4$	33.8 101.7	33.7 101.7
V	$NaVO_3$	23.5 71.7	23.5 71.5

TABLE XI

CHROMOMETRY

Element	Sample formula	Element mg.	
		Content	Found
Br	NaBrO	37.6 112.7	37.2 112.2
Ce	$Ce(SO_4)_2$	56.2 170.8	55.9 170.5
Cr	K_2CrO_4	26.2 78.6	26.2 78.5
Fe	$Fe_2(SO_4)_3$	10.6 59.1	10.3 58.8
I	KI_3	67.8 202.4	67.5 201.6
Mn	$KMnO_4$	33.8 101.7	33.7 101.7
V	$NaVO_3$	16.1 49.1	15.8 48.7

(*L*) *Vanadyl sulfate method* (MnO_4^-, CrO_4^{2-}, Ce^{4+}). Permanganate is the only ion determinable by direct titration. For chromate and cerium(IV) sulfate, an excess of vanadyl sulfate is added and back-titrated with standard iron(III) sulfate solution (Table XII).

TABLE XII

VANADYL SULFATE METHOD

Element	Sample formula	Element mg.	
		Content	Found
Ce	$Ce(SO_4)_2$	56.2 170.8	56.9 170.6
Cr	K_2CrO_4	26.2 78.6	26.0 78.0
Mn	$KMnO_4$	37.3 110.9	37.2 110.7

(*M*) *Mixture of chromate and iron(III)*. Chromate is reduced with chromium(II) solution; indigo carmine is decolorized at the end point and used as indicator. Total concentration of chromate and iron (III) is determined by the titration using crystal violet as indicator which is reduced by the standard solution with more difficulty than iron(III); iron is estimated from the difference between these two titrations (Table XIII).

TABLE XIII

MIXTURE OF IRON(III) AND CHROMATE

0.0921 N $CrSO_4$ required ml. $Na_5P_3O_{10}$ as masking agent		Cr mg.		Fe mg.	
Indigo carmine	Crystal violet	Content	Found	Content	Found
5.47	8.94	26.2	26.1	19.6	19.5
5.45	15.96	26.2	26.0	59.2	58.9
10.93	17.86	52.6	52.2	59.1	58.9
16.39	19.01	78.6	78.2	19.6	19.0
16.42	23.35	78.6	78.4	39.4	39.0

(*N*) *Mixture of vanadate and iron(III)*. Indigo carmine is used as indicator in the chromometric titration of vanadate; the total concentration of these two components is determined by the use of neutral red as indicator. (Table XIV).

TABLE XIV

MIXTURE OF IRON(III) AND VANADATE

0.0921 N $CrSO_4$ solution required $Na_5P_3O_{10}$ as masking agent		V mg.		Fe mg.	
Indigo carmine	Neutral red	Content	Found	Content	Found
2.42	5.21	15.6	15.1	19.6	19.1
2.43	11.04	15.6	15.1	59.1	58.8
4.99	13.59	31.2	31.1	59.1	58.8
7.46	10.25				
7.44	13.14	46.9	46.5	39.4	39.0

Summary

Antimony(III), arsenic(III), chromium (II), iron(II), molybdenum(V), selenium (IV), thallium(I), titanium(III) and vanadium(IV) are titrated in neutral solutions with oxidizing standard solutions, chromate, bromate, hypobromite, permanganate, and vanadate solution, in the presence of triphosphate. A few of these elements, chromium(II), iron(II), titanium(III) and vanadium(IV) in their mixture are also determined.

On the other hand, cerium(IV), hypobromite, chromate, triiodide, permanganate, vanadate and hydrogen peroxide, are titrated with reducing standard solutions, chromium(II), iron(II), titanium(III), and vanadyl solution containing triphosphate. Some of them in mixtures are also determined.

The authors wish to express their hearty thanks to Professor Matsusuke Kobayashi for his valuable advice and encouragement throughout this study.

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