

## Oxidation of Low Valent Sulphur Compounds with Lead Tetraacetate: Part II—Potentiometric Determination of Pb(IV) Acetate by Reduction with Thiosulphate or Metabisulphite

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Lead tetraacetate is reduced quantitatively by thiosulphate or metabisulphite solution. As little as 0.14 mg of Pb(IV) can be estimated by potentiometric titration in glacial acetic acid medium. The titration proceeds fast and the end point is marked by a large potential jump. The oxidation products when  $S_2O_3^{2-}$  is used as titrant, have been identified as di- and tetrathionates, whereas sulphate is the end product in titrations using  $S_2O_8^{2-}$ .

EARLIER we studied<sup>1</sup> the reaction between lead tetraacetate and bisulphite ( $HSO_3^-$ ) potentiometrically and evolved methods for the determination of  $\sim 0.16$  mg of  $HSO_3^-$  in the direct titration and  $\sim 0.43$  mg of Pb(IV) in the inverse titration.

Presently the reaction between  $Pb(Ac)_4$  and  $S_2O_3^{2-}$  and  $S_2O_8^{2-}$  has been studied potentiometrically with a view to finding out if the quantitative course of the reaction can be used for a direct potentiometric determination of Pb(IV) acetate.

### Materials and Methods

Lead tetraacetate was prepared and standardized as given before<sup>1</sup>.

Sodium thiosulphate and metabisulphite solutions were prepared from the Analar product and standardized according to recommended procedures<sup>2</sup>.

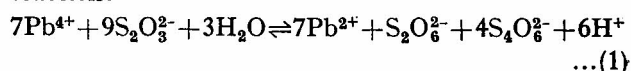
Other reagents were of analytical grade (E. Merck or BDH). Doubly distilled water was used for the preparation of solutions.

Platinum electrode in combination with SCE was used for e.m.f. measurements on a direct reading millivoltmeter. The titrations were performed at room temperature ( $\sim 22^\circ$ ).

### Results and Discussion

Owing to the instability of thiosulphate and metabisulphite in acid solutions the direct titration of these reducing agents with Pb(IV) acetate cannot be carried out successfully. The titration was performed in the presence of acetate buffer, and to pH of the titration medium being adjusted by the addition of the appropriate amounts of 1M NaOH throughout the titration process. The results obtained, however, were not reliable due to the complexity of the oxidation products. In addition, the end point was highly affected by the slight changes in the acidity of the medium. The reaction became very sluggish near the end point. These drawbacks restricted the scope of the method to the titration of Pb(IV) acetate only with the reducing material.

*Titration of Pb(IV) acetate with thiosulphate*—On titrating amounts of Pb(IV) acetate ranging from 0.28-140 mg with  $S_2O_3^{2-}$  solution the curves obtained are characterized by a single large inflection which amounts to 100 mV/0.02 ml of titrant. The reaction proceeds very fast at the start but near the end point it becomes less rapid and needs  $\sim 2$  min to attain equilibrium. From the amount of thiosulphate consumed at the equivalence point it is concluded that  $S_2O_3^{2-}$  is oxidized according to the overall reaction:



The formal values of the equilibrium constant ( $K$ ) and the extent of completion ( $\alpha$ ) for reaction (1) are to  $1 \times 10^{19}$  and  $1 \times 10^{19}$  respectively indicating the quantitative nature of the reaction.

The formation of di- and tetrathionate as a result of the oxidation process was confirmed by recording the spectra of the titrated solution both prior to and at the equivalence point. The solution exhibited in each case two absorption bands at 242 nm and 318 nm characteristic of  $S_2O_8^{2-}$  and  $S_4O_6^{2-}$  anions respectively.

The formation of dithionate was also confirmed as follows:

At the end point in a series of titrations at different concentrations of Pb(IV) acetate, the Pb(II) produced was precipitated out as lead sulphate by adding dilute sulphuric acid. The dithionate in the filtrate was then determined according to Murthy<sup>3</sup> by treating the filtrate with alkaline permanganate which destroys tetrathionate. The excess permanganate was then removed by boiling with manganous sulphate, the solution filtered and the dithionate in the filtrate oxidized with standard dichromate in acid medium. The excess dichromate was back titrated iodometrically.

As is evident from the data included in Table 1, the titration of Pb(IV) acetate with  $S_2O_3^{2-}$  can be used as an analytical method for the microdetermination of amounts as small as 0.13 mg of Pb(IV).

TABLE 1 — RESULTS OBTAINED FOR THE POTENTIOMETRIC TITRATION OF Pb(IV) ACETATE WITH  $S_2O_5^{2-}$ 

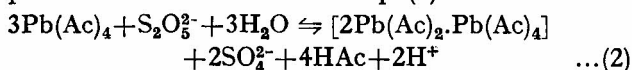
(The titrations were performed in 50 ml glacial acetic acid)

Amount of Pb(Ac) <sub>4</sub> titrated			End point (ml)		Error Inflection (%) (±)	at end point (mV/0.02 ml of titrant)
ml	mg	mg of Pb(IV)	Theor.	Exp.		
TITRATION OF $4.2 \times 10^{-2} N$ Pb(IV) ACETATE WITH $2.2 \times 10^{-2} M$ $S_2O_5^{2-}$						
2	18.614	8.698	2.44	2.44	Nil	100
5	46.535	21.745	6.1	6.08	0.33	100
8	74.456	34.792	9.76	9.75	0.1	95
10	93.07	43.49	12.2	12.16	0.33	92
15	139.605	65.235	18.3	18.2	0.54	86
TITRATION OF $7.5 \times 10^{-3} N$ Pb(IV) ACETATE WITH $2.5 \times 10^{-3} M$ $S_2O_5^{2-}$						
2	3.324	1.548	3.86	3.85	Nil	92
5	8.310	3.870	9.65	9.64	0.1	95
8	13.296	6.192	15.44	15.4	0.26	90
TITRATION OF $1.25 \times 10^{-3} N$ Pb(IV) ACETATE WITH $6.4 \times 10^{-4} M$ $S_2O_5^{2-}$						
1	0.277	0.129	1.26	1.26	Nil	98
2	0.554	0.258	2.52	2.50	0.79	95
4	1.108	0.516	5.04	5.02	0.4	92
6	1.662	0.774	7.56	7.54	0.26	92
10	2.770	1.290	12.6	12.56	0.32	90

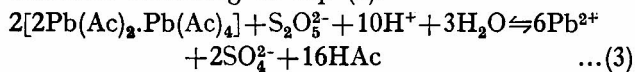
*Titration of Pb(IV) acetate with metabisulphite* —

The potentiometric titration curves obtained by titrating varying amounts of lead tetraacetate with  $S_2O_5^{2-}$ , are characterized by two inflections. The first of these occurs much later than the one corresponding to Pb(III) step (Fig. 1). It may be attributed to the formation of a mixed acetate complex ( $2Pb^{2+} \cdot Pb^{4+}$ )(Ac)<sub>8</sub> by the interaction of  $Pb^{2+}$  and the remainder of  $Pb^{4+}$  in solution<sup>1</sup>.

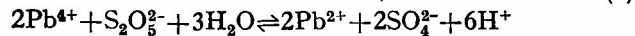
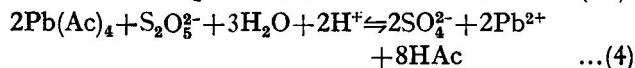
The reaction at the first inflection is expected to proceed in accordance with Eq. (2):



The intermediate reduction product seems to be further reduced to divalent lead at the second inflection according to Eq. (3).



The overall reaction at the second end point seems to take place in accordance with Eq. (4) which can be used in the quantitative determination of Pb(IV).



The values of the equilibrium constant ( $K$ ) and degree of completion ( $\alpha$ ) for this reaction, as obtained from the titration curves are  $1.4 \times 10^{27}$  and  $1.2 \times 10^9$  respectively.

Amounts of Pb(IV) up to 50 mg can be titrated with  $S_2O_5^{2-}$  in glacial acetic acid medium with reasonable accuracy. At higher concentrations of

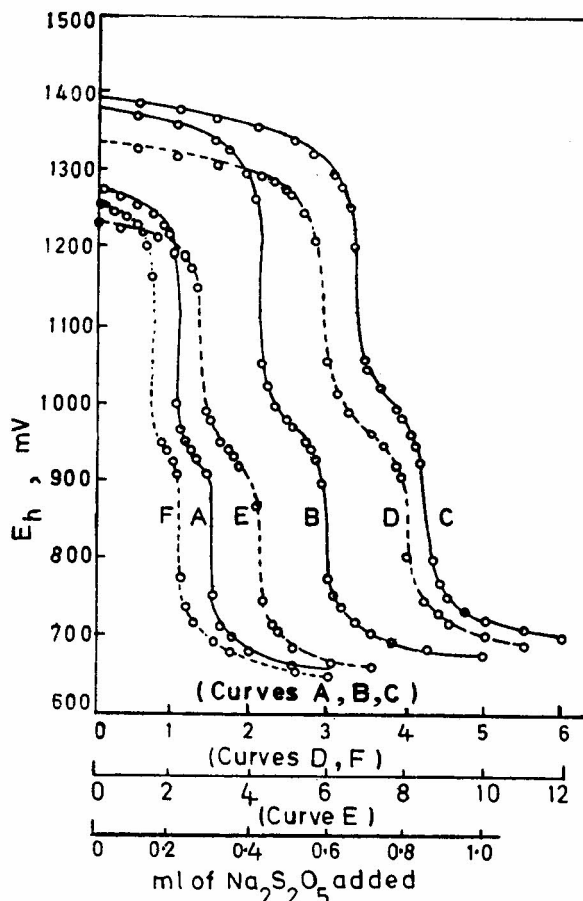


Fig. 1 — Titration of Pb(IV) acetate with  $Na_2S_2O_5$  [(A) Titration of 5 ml of  $4.88 \times 10^{-2} N$   $Pb(Ac)_4$  with  $4.07 \times 10^{-2} M$   $S_2O_5^{2-}$ ; (B) titration of 10 ml of  $4.88 \times 10^{-2} N$   $Pb(Ac)_4$  with  $0.07 \times 10^{-2} M$   $S_2O_5^{2-}$ ; (C) titration of 15 ml of  $4.88 \times 10^{-2} N$   $Pb(Ac)_4$  with  $4.07 \times 10^{-2} M$   $S_2O_5^{2-}$ ; (D) titration of 10 ml of  $1.22 \times 10^{-3} N$   $Pb(Ac)_4$  with  $3.81 \times 10^{-3} M$   $S_2O_5^{2-}$ ; (E) titration of 1 ml of  $1.4 \times 10^{-3} N$   $Pb(Ac)_4$  with  $8.3 \times 10^{-4} M$   $S_2O_5^{2-}$ ; and (F) titration of 5 ml of  $1.4 \times 10^{-3} N$   $Pb(Ac)_4$  with  $8.3 \times 10^{-4} M$   $S_2O_5^{2-}$ ]

Pb(IV) the second end point which corresponds to the completion of the reduction process occurs earlier than the expected value due to the incomplete decomposition of the mixed complex formed at the first inflection.

The data given in Table 2 show that the method can be applied for the microdetermination of amounts as small as 0.14 mg of Pb(IV). The inflection at the second end point which is used in the quantitative determination of lead(IV) decreases as the concentration of  $Pb(Ac)_4$  solution increases. The reaction is very rapid at the early stages of the titration but becomes less rapid as the second end point is approached needing  $\sim 2$  min for the establishment of equilibrium.

Oxidation of low valent sulphur compounds usually ends up into sulphate ion when the oxidation is carried out with alkaline permanganate<sup>4-6</sup>, except in the oxidation of sulphide in the presence of telluric acid when dithionate is obtained as oxidation product<sup>7</sup>. In oxidation in acid medium the formation of dithionate is frequently encountered with sulphide, sulphite and thiosulphate<sup>8</sup>.

TABLE 2 — RESULTS OBTAINED FOR THE POTENTIOMETRIC TITRATION OF Pb(IV) ACETATE WITH  $S_2O_5^{2-}$ 

(The titrations were performed in 50 ml glacial acetic acid)

Amount of Pb(Ac) <sub>4</sub> titrated			End point* (ml)		Error (%. ±)	Inflection at end point* (mV/0.02 ml of titrant)
ml	mg	mg of Pb(IV)	Theor.	Exp.		
TITRATION OF $4.88 \times 10^{-2} N$ Pb(IV) ACETATE WITH $4.07 \times 10^{-2} M$ $S_2O_5^{2-}$						
3	32.45	15.164	0.9	0.9	Nil	18
5	54.09	25.276	1.5	1.49	0.66	15
8	86.55	40.445	2.4	2.38	0.83	12
10	108.18	50.552	3.0	2.98	0.66	12
15	162.27	75.828	4.5	4.28	4.88	10
TITRATION OF $1.22 \times 10^{-2} N$ Pb(IV) ACETATE WITH $3.81 \times 10^{-3} M$ $S_2O_5^{2-}$						
2	5.41	2.528	1.6	1.6	Nil	22
4	10.82	5.056	3.2	3.18	0.62	20
10	27.05	12.64	8.0	8.0	Nil	18
12	32.46	15.168	9.6	9.57	0.31	16
TITRATION OF $1.4 \times 10^{-3} N$ Pb(IV) ACETATE WITH $8.3 \times 10^{-4} M$ $S_2O_5^{2-}$						
1	0.31	9.145	0.42	0.42	Nil	25
2	0.62	0.290	0.84	0.85	1.19	22
5	1.55	0.725	2.1	2.12	0.95	20
10	3.1	1.450	4.20	4.20	Nil	20
15	4.65	2.175	6.3	6.26	0.63	18

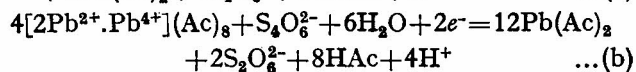
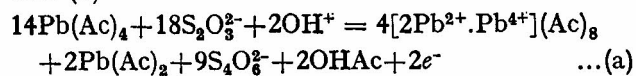
\*At the second reduction step.

Metabisulphite solution is found to be oxidized to sulphate with  $Br_2$ , iodine, alkaline permanganate<sup>9</sup> or acid permanganate in the presence of fluoride ions<sup>10</sup>. Thiosulphate solution is oxidized to tetrathionate ( $S_4O_6^{2-}$ ) or sulphate ions with many oxidizing agents.

In the present investigation the oxidation of thiosulphate with lead tetraacetate initially leads to the formation of tetrathionate as an oxidation product while the oxidising agent is reduced to the intermediate reduction product  $[2Pb^{2+}.Pb^{4+}](Ac)_8$  and divalent lead ions. The mixed acetate complex appears throughout the titration process as a slight white turbidity which vanishes completely within few seconds due to its reduction to divalent lead

by tetrathionate present in solution. The tetrathionate, in turn is partially oxidized to dithionate.

From the quantities reacting at equivalence point at the optimum conditions, it is concluded that  $S_2O_5^{2-}$  is oxidized with  $Pb(Ac)_4$  to di- and tetrathionate and the net reaction can be represented by Eq. (1): Eq. (1) is based on the two partial reactions (a) and (b)



Reaction (b) seems to be very fast as evidenced by the rapid dissociation of the mixed acetate complex. Accordingly the formation of the latter is readily terminated and consequently only one inflection is exhibited in the titration curves of  $Pb(Ac)_4$  with  $S_2O_5^{2-}$ .

When lead tetraacetate is titrated with  $S_2O_5^{2-}$  or  $HSO_3^-$  (ref. 1) the intermediate acetate complex, is stabilized in solution because of the absence of any reducing species in the titration medium. The reducing agents are oxidized in such cases to sulphate ions. The mixed acetate complex is only affected, i.e. converted to divalent lead, when the required amount of the reducing agent (titrant) is added to the attainment of the second end point. This fact reflects itself in the appearance of the second inflection.

## References

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