In weak solutions with ferric chloride neither α-oxan, nor β-oxan salts give a precipitate.

Calcium salts both of α-oxan and of β-oxan are amorphous, gelatinous substances. Compared with calcium carbonate they are much more soluble in water (up to 1 gram to a liter).

The sodium salt of α-oxan like sodium carbonate forms with manganous chloride ($MnCl_2$) an abundant white precipitate, while under the same conditions the sodium salt of β-oxan gives no precipitate. Aluminium chloride acts in the same manner with the difference that the precipitates formed from sodium carbonate and sodium α-oxanate salts, decompose with elimination of gases; but the sodium salt of β-oxan under the same conditions and at the same dilution (2.5 grams to 250 cc. of water) does not give a precipitate and does not eliminate gas. Both the salts of α-oxan and the salts of β-oxan in time lose, in a larger or smaller degree, the property of eliminating gas, or in other words the quantity of gas eliminated diminishes. This fact is more sharply pronounced in β-oxan salts. This property is most probably due to polymerization and may be dependent upon the presence of certain admixtures acting as catalyzers, for in certain cases it is more pronounced than in others.

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THE INFLUENCE OF LEAD ON THE FERROCYANIDE TITRATION OF ZINC.

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Of all the volumetric methods for the determination of zinc in ores, the procedure as outlined in the "Modified Waring Method"[1] is by far the most satisfactory for complex ores. The principal service which this method renders is the removal of all of the heavy metals which interfere with the ferrocyanide titration. In many zinc ores, notably those from the Mississippi Valley, the heavy metals which thus interfere are absent, hence the separations called for in this method can be materially simplified.

While it is universally acknowledged that iron must not be present in the ferrocyanide titration for zinc, the influence of lead has been a much mooted question. Béringer[2] gives quantitative data to show that lead gives a higher result. Seaman[3] gives data to show the bad influence of lead. Stone[4] is of the opinion that lead alone need not be separated, but that if the lead be present the solution must be quite strongly acid. Miller[5] indicates conditions which allow for the presence of lead.

[1] THIS JOURNAL, 29, 265 (1907).

[2] Béringer, "Text-book of Assaying."

[3] THIS JOURNAL, 29, 207 (1907).

[4] *Ibid.*, 17, 475, 476 (1895).

[5] Miller, "Quantitative Analysis for Mining Engineers."

With this brief résumé of the various statements as to the effect of lead on the ferrocyanide titration for zinc, attention should be directed to the ferrocyanide method for lead itself, as described by its originator Low.[1] In this method the titration of lead acetate is carried out in a solution containing about $2^1/_2\%$ free acetic acid. While Low does not, in his latest description of the method, specifically state that free mineral acids should not be present, yet from the procedure as outlined, namely, solution of lead carbonate in dilute acetic acid, it is inferred that free mineral acid would not be present. As a matter of fact, our experience with the method seems to show that free mineral acids must be absent in the ferrocyanide titration for lead. In other words, even a very small amount of free nitric or hydrochloric acid prevents the formation of lead ferrocyanide, which would render the method worthless.

Galletti,[2] who devised the ferrocyanide titration for zinc, worked in acetic acid solution. He used no indicator to obtain the endpoint. Fahlberg[3] later showed the efficiency of the method in hydrochloric acid solution, using uranium nitrate as an outside indicator, which is the method commonly used to-day.

A number of series of experiments have been made, the conditions being varied as to the character of the liquid titrated.

Lead acetate was titrated with potassium ferrocyanide in the diluted acetic acid solution as recommended by Low. The temperature of titration was 65° and the solution had a volume of 200 cc.

TABLE I.

Pb present. Gram.	HCl present. Per cent.	Pb found. Gram.	
0.1947	none	0.1947	
0.1947	0.0125	0.1947	
0.1947	0.025	0.1947	
0.1947	0.125	0.1921	Difference dependent to some extent on temperature.
0.1947	0.125	0.1867	
0.1947	0.25	0.0000	
0.1947	0.75	0.0000	

It is apparent that free hydrochloric acid present up to one-eighth of 1% does not notably affect the lead determination, but when present in quantity as high as 1% no lead ferrocyanide is precipitated and no lead is indicated.

Precisely the same order of results occurs when a chloride is added to the acetic acid solution.

It is obvious that the presence of hydrochloric acid or small quantities of chlorides renders worthless the ferrocyanide titration for lead.

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[1] THIS JOURNAL, **15**, 550 (1893).

[2] *Z. anal. Chem.*, 4, 213.

[3] *Ibid.*, **13**, 379.

TABLE II.

Pb present. Gram.	NH_4Cl present. Gram.	Pb found. Gram.
0.1947	none	0.1947
0.1947	0.1	0.1951
0.1947	0.5	0.1947
0.1947	1.0	0.1938
0.1947	3.0	0.035–0.088[1]
0.1949	5.0	0.0000

In the titration of lead by the ferrocyanide method, a solution of uranium acetate is by far the best indicator. The nitrate is unsuitable, inasmuch as it invariably contains free acid.

Mixtures of varying amounts of zinc and lead acetates were titrated in the presence of different amounts of hydrochloric acid and ammonium chloride.

TABLE III.

Acetate solutions of lead and zinc titrated at 70° in a volume of 200 cc. in presence of 10 grams NH_4Cl and 3 cc. HCl.

Zn present. Gram.	Pb present. Gram.	Zn found. Gram.	Error. Gram.
0.2000	0.0000	0.2000	....
0.2000	0.0431	0.2010	+0.0010
0.1500	0.0862	0.1512	+0.0012
0.1000	0.1292	0.1005	+0.0005
0.0500	0.1723	0.0498	—0.0002
0.0000	0.1758	0.0005	+0.0005

TABLE IV.

Solutions of acetates titrated at 70° in a volume of 200 cc. in presence of 10 grams NH_4Cl and 6 cc. HCl.

Zinc present. Gram.	Lead present. Gram.	Zinc found. Gram.	Error. Gram.
0.2000	0.0000	0.2000	..
0.2000	0.0431	0.2000	..
0.1500	0.0862	0.1502	+0.0002
0.1000	0.1292	0.1005	+0.0005
0.0500	0.1723	0.0498	—0.0002
0.0000	0.1723	0.0005	+0.0005

TABLE V.

Solutions of acetates titrated at 70° in a volume of 200 cc. in presence of 10 grams NH_4Cl and 12 cc. HCl.

Zn present. Gram.	Pb present. Gram.	Zn found. Gram.	Error. Gram.
0.2000	0.0000	0.2000	..
0.2000	0.0431	0.2005	+0.0005
0.1500	0.0862	0.1506	+0.0006
0.1000	0.1292	0.1003	+0.0003
0.0500	0.1723	0.0504	+0.0004
0.0000	0.1723	..	..

[1] Results differing due to temperature change.

A number of experiments were next made using solutions containing chlorides only.

Table VI.

In this group of experiments the amount of hydrochloric acid present was varied. All of the solutions were titrated at 70°, had a volume of 200 cc. and contained 10 grams NH_4Cl.

Zinc present. Gram.	Lead present. Gram.	Zinc found. Gram.	Free HCl present. Per cent.	Error. Gram.
0.1000	0.1133	0.1001	0.0	+0.0001
0.1000	0.1133	0.0999	0.12	—0.0001
0.1000	0.1133	0.1002	0.25	+0.0002
0.1000	0.1133	0.1002	0.75	+0.0002
0.1000	0.1133	0.1000	1.00	0.0000
0.1000	0.1133	0.1001	1.25	+0.0001
0.1000	0.1133	0.0998	1.50	—0.0002
0.1000	0.1133	0.1001	2.25	+0.0001
0.1000	0.1133	0.1006	3.00	+0.0006
0.1000	0.1133	0.1004	6.00	+0.0004
0.1000	0.1133	0.0991	12.00	—0.0009

With large amounts of free hydrochloric acid present, that is, from 12 to 18%, it is impossible to obtain a definit endpoint. When no free acid or as little as $^1/_4$%, is present, the true endpoint in the titration is a matter of considerable uncertainty. An apparent endpoint appears, but by continued stirring disappears. This false endpoint is due to the hydrosol form of the colloidal zinc ferrocyanide, which with insufficient free acid goes only slowly into the hydrogel form. The true endpoint is quickly reached with 1$^1/_2$% of free hydrochloric acid and is distinct up to as much as 6% free acid.

From Table VI it is apparent in general in the presence of a material amount of free hydrochloric acid that the presence of lead would never be discovered in the ferrocyanide titration for zinc.

Table VII

Volume of solution 200 cc. Ten grams of ammonium chloride, and 1.5% free hydrochloric acid present. Titrations made at 70°.

Zinc present. Gram.	Lead present. Gram.	Zinc found. Gram.	Error. Gram.
0.1000	0.2266	0.1002	+0.0002
0.1000	0.3399	0.1005	+0.0005
0.1000	0.4532	0.1005	+0.0005
0.1000	0.5665	0.1007	+0.0007
0.1000	0.6798	0.1005	+0.0005
0.1000	0.7931	0.1005	+0.0005
0.1000	0.9064	0.1005	+0.0005
0.1000	1.0197	0.1010	+0.0010
0.1000	1.117	0.1003	+0.0003
0.1000	2.234	0.1003	+0.0003
0.1000	3.352	0.1005	+0.0005
0.1000	3.724	0.1003	+0.0003

In the above experiments successively larger amounts of lead chloride have been added.

In our experience the quantity of ammonium chloride necessary to have present can be anywhere from 1 to 20 grams in a 200 cc. solution. When excessively large amounts are present, 40 grams or more, the endpoint becomes indistinct.

Various indicators have been suggested from time to time to determin the endpoint in the ferrocyanide titration for zinc. Our experiments suggest that a 0.9% ammonium molybdate solution is the most delicate of the various indicators proposed, but that it is not widely applicable. Glacial acetic acid, 5% sodium tungstate, cobalt nitrate, hydrochloroplatinic acid, are fair indicators, but not as delicate as uranium nitrate or ammonium molybdate. Of all the indicators used, the 5% solution of uranium nitrate is very delicate and reliable.

Conclusions.

In the ferrocyanide titration for zinc as commonly carried out, lead is without influence.

The ferrocyanide titration for lead should be carried out in acetic acid solution and the mineral acids must be absent.

In the technical examination of ores for zinc where lead and iron are the only heavy metals present to an appreciable extent, and such is the case with the Wisconsin zinc ores, it is unnecessary to remove the lead for the ferrocyanide titration for zinc. Half-gram samples of the ore can be dissolved in 10 cc. of concentrated hydrochloric acid with the addition of a little nitric acid. To the solution after dilution, ammonium hydroxide is added and the ferric hydroxide and insoluble matter are removed by filtration. The precipitate is dissolved in dilute hydrochloric acid and reprecipitation by ammonia is effected, the filtrates being united. The solution should now be acidified with hydrochloric acid and when evaporated somewhat is ready to be titrated.

For titration the solution must be hot, it should have a volume of 200 cc., should contain 6–10 cc. concentrated hydrochloric acid and 10 grams of ammonium chloride. The ferrocyanide solution should be of such strength that 1 cc. = 0.005 gram zinc, and the best indicator is a 5% solution of uranium nitrate.

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A NEW COLORIMETRIC METHOD FOR TITANIUM.

BY VICTOR LENHER AND W. G. CRAWFORD.

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The estimation of titanium is commonly considered by chemists as one of the more troublesome determinations. The methods most widely