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The effect of insoluble sulphates on the volumetric determination of lead

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THE EFFECT OF INSOLUBLE SULPHATES ON THE VOLUMETRIC
DETERMINATION OF LEAD

by

Mervin Joe Kelly

and

Ralph Knappenberger.

A

T H E S I S .

submitted to the faculty of the
SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI
in partial fulfillment of the work required for the

D E G R E E S O F
BACHELOR OF SCIENCE IN METALLURGY


and

BACHELOR OF SCIENCE IN GENERAL SCIENCE.

Rolla, Mo.

1913.

Approved by



Professor of Chemistry.

15681

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INTRODUCTION.

It has been pointed out that Alexander's Molybdate Method for lead gives inconsistently varying results when calcium is present in the ore. Low-- Technical Method of Ore Analysis, 5th Edition, page 152--says:- "Calcium forms a molybdate which is more or less insoluble under the conditions of the titration and tends to raise the results in an irregular manner." Furman and Pardoe--Manual of Practical Assaying, 7th Edition, page 156--say:- "If calcium is present in the ore it must be removed, as it forms a molybdate on titration which is not entirely soluble under the conditions of the titration. Irving Bull--School of Mines Quarterly, Volume 23, page 348--gives the result of a number of experiments with lead and varying amounts of calcium, which show no variations due to the presence of calcium, even when the amount of calcium is twice the amount of lead. It was to clear up this apparent contradiction and to find the true effect of the presence of calcium on the titration in the molybdate method, that this investigation was started.

- II -

EXPERIMENTAL.

(a) Preliminary Runs.

The method first employed was to take a lead solution of known strength, add varying amounts of calcium, and run this solution for lead according to the regular Alexander method.

The following solutions were employed;-

A lead nitrate solution containing .005 grams Pb per c.c.

Ammonium molybdate solution equivalent to .005 grams Pb per c.c. The solution was standardized against c.p. Pb SO₄.

Calcium chloride solution containing .005 grams CaO per c.c.

Tannic acid solution (1 - 300).

Fifty c.c. of the Pb (NO₃)₂ solution was taken each time and varying amounts of Ca Cl₂ added. The solution was taken down until all the water was evaporated off, allowed to cool and 10 c.c. of H₂ SO₄ (Sp.Gr.1.84) added and taken down over a free flame to copious SO₃ fumes. This was allowed to cool, diluted to 75-100 c.c. with cold water and filtered through a fine filter paper. The sulphates were washed five times with (1 - 10)

H_2SO_4 and two or three times with alcohol. The filter paper containing the sulphates was placed in a beaker, $NH_4 C_2 H_3 O_2$ and 20 - 30 c.c. water added. This was boiled gently until all the sulphates were dissolved, more $NH_4 C_2 H_3 O_2$ and water being added, if necessary. After the sulphates were dissolved, the solution was diluted to 150 c.c., 3 - 4 c.c. $H_2 C_2 H_3 O_2$ added, brought to a boil and titrated with the standard solution of $(NH_4)_2 Mo O_4$ until the first brown color was reached, tannic acid being used as indicator.

Table 1 tabulates the results obtained.

Lead	Ca O	$(NH_4)_2 Mo O_4$ No. c. c. of .005 solution.	
Milligrams	Milligrams	Kelly	Knappenberger
250	000	50.00	50.00
250	500	53.80	-----
250	250	51.74	52.12
250	250	51.36	51.75
250	200	51.40	51.30
250	200	52.10	51.17
250	150	52.31	51.52
250	150	51.50	51.94
250	100	52.90	53.05
250	100	52.80	51.75
250	50	51.50	52.11
250	50	51.10	50.94

As is shown in Table 1, high results were obtained, which varied in an irregular manner, the percentage excess being in no way proportional to the amount of calcium present. But this was to be expected, due to the number of variables present. Due to the ~~insolubility~~ solubility of Ca SO_4 in water and in dilute H_2SO_4 , the amount of calcium present when the solutions were titrated was much less than the amount added, and the amounts less in the various instances were not proportional, due to the difference in treatment received by each, such as amount of washing, dilution etc. The amount of $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ present in each also varied somewhat. The Ca SO_4 was so difficult to dissolve in the $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ that much more was added when the amount of calcium was high.

(b) The effect of ammonium acetate on the solubility of the lead molybdate.

To determine the effect of $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ alone on the titration, when no calcium was present, a $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ solution containing .005 grams of Pb per c.c. was made up, and 50 c.c. of this solution was run with varying amounts of the $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$.

The results obtained are tabulated in Table 2.

Table 2.

Pb Milligrams	NH ₄ C ₂ H ₃ O ₂ Grams	(NH ₄) ₂ Mo O ₄ No.c.c. of .005 solution	
		Kelly	Knappenberger
250	0.00	50.0	50.0
250	5.00	50.0	50.0
250	10.00	50.0	50.1
250	15.00	50.0	50.0
250	25.00	50.0	50.0
250	30.00	50.0	50.0

As is seen from Table 2, NH₄C₂H₃O₂, even when present to near saturation, has no solvent effect on the lead molybdate found.

With the large amounts of NH₄C₂H₃O₂, the end points were not good and the volume of solution to be titrated had to be increased.

(c) Determination of solubility of calcium molybdate under conditions of titration.

To determine whether calcium, when present alone in solution, would form an insoluble molybdate under the conditions of the titration, the following experiments were made: The Ca Cl₂ solution was neutralized with NH₄OH, 3 - 4 c.c. HC₂H₃O₂ added and (NH₄)₂ Mo O₄ passed into the solution until the first brown tinge ap-

peared in the indicator.

The results obtained are tabulated in Table 3.

Table 3.

Ca O Milligrams	(NH ₄) ₂ Mo O ₄ No. c.c. of .005 solution
125	.40
250	.40
500	.40

The results of Table 3 show, since .4 is the blank for the standard used, that in a hot slightly acid acetate solution no insoluble calcium molybdate is formed.

(d) The effect of calcium on the titration with no NH₄C₂H₃O₂ present.

To determine the effect of calcium on the titration when lead was present, but no NH₄C₂H₃O₂, the following experiments were performed:-

A constant amount of Pb (C₂H₃O₂)₂ was taken and variable amounts of Ca Cl₂ added, NH₄OH added drop by drop until the slight amount of free acid in the Ca Cl₂ solution was neutralized, then 3 - 4 c.c. HC₂H₃O₂ added. The solution was brought to a boil and titrated with the (NH₄)₂ Mo O₄ solution. While there is some NH₄C₂H₃O₂ present, due to the few drops of NH₄OH added, it is so

slight it can be considered to have no effect.

The results obtained are tabulated in Table 4.

Table 4.

Pb Milligrams	Ca O Milligrams	(NH ₄) ₂ Mo O ₄ No. c. c. of .005 solution	
		Kelly	Knappenberger
250	000.0	50.	50.0
250	500.0	55.90	54.80
250	400.0	53.94	53.75
250	400.0	55.20	54.00
250	300.0	54.72	54.06
250	300.0	54.39	53.90
250	200.0	54.17	53.80
250	200.0	54.10	54.00
250	100.0	53.61	53.60
250	100.0	53.50	53.55
250	50.0	53.15	53.20
250	25.0	52.28	52.40
250	10.0	51.40	51.35
250	7.5	50.80	50.90
250	5.0	50.50	50.40
250	2.5	50.35	50.30

(e) The effect of barium in the titration with ^{no}ammonium acetate present.

A Ba Cl₂ solution containing .005 grams Ba O per

c.c. was used and the effect of the barium upon the titration was determined in the same manner as for Ca O.

Table 5 shows the results obtained.

Table 5.

Pb Milligrams	Ba O Milligrams	(NH ₄) ₂ Mo O ₄ No.c.c. of .005 solution.
		Kelly
250	000	50.00
250	500	64.50
250	400	65.82
250	300	62.12
250	200	62.40
250	100	58.86
250	50	57.59
250	25	54.57
250	15	53.27
250	10	52.70
250	5	51.67

From the results shown in Table 4 and 5, it is evident that high results are obtained when calcium or barium are present. It also shows that the increase in the number of c.c.'s used and the amount of calcium or barium present, are proportional in a very consistent manner up to 100 milligrams, then an increase in the

amount of Ca O or Ba O present seems to have a small and very irregular effect. From the results it seems that complex molybdates of calcium and lead and barium are formed, which cause the use of much more molybdate and hence the high result.

The inconsistencies in variations when no more than 100 milligrams of Ba O or Ca O are present cannot be readily explained, but it seems, from observations made on the different experiments, that such factors as heat, rapidity of adding the molybdate, and the solubility of the molybdate formed causes these variations.

(f) The effect of ammonium acetate on the titration with constant amounts of lead and calcium.

The next step was to determine the solvent effect, if any, of $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ on the calcium lead molybdates formed. Constant quantities of the $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ solution and CaCl_2 solution were taken, neutralized with NH_4OH , the $\text{Pb}(\text{OH})_2$ formed being dissolved in $\text{HC}_2\text{H}_3\text{O}_2$ and the solution titrated in the usual way.

Table 6 shows results obtained.

Table 6.

Pb Milligrams	Ca O Milligrams	$\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ Grams	$(\text{NH}_4)_2\text{MoO}_4$ No. c. c. of .005 solution
250	200	00.0	Knappenberger 54.60
250	200	5.0	54.48
250	200	10.0	53.41
250	200	15.0	52.35
250	200	20.0	51.16
250	200	25.0	49.63
250	200	30.0	48.50

Pb Milligrams	Ca O Milligrams	$\overset{6 a}{\text{NH}_4\text{C}_2\text{H}_3\text{O}_2}$ Grams	$(\text{NH}_4)_2\text{MoO}_4$ No. c. c. of .005 solution
250	100	00.0	Kelly 53.73
250	100	5.0	53.60
250	100	10.0	53.18
250	100	15.0	52.45
250	100	20.0	51.50
250	100	25.0	50.95
250	100	30.0	46.65

6 b

Pb Milligrams	Ca O Milligrams	NH ₄ C ₂ H ₃ O ₂ Grams	(NH ₄) ₂ Mo O ₄ No.c.c. of .005 solution
250	50	00.0	Knappenberger 53.50
250	50	5.0	53.35
250	50	10.0	52.65
250	50	15.0	51.55
250	50	20.0	50.84
250	50	25.0	48.90
250	50	30.0	48.30

From Table 6 it is apparent that NH₄C₂H₃O₂ has a solvent effect on the compound formed when calcium is present. This solubility varies in a very rough manner with the amount of NH₄C₂H₃O₂ present. That is, the more NH₄C₂H₃O₂ we have present the less the number of c.c. of (NH₄)₂Mo O₄ required. With the 50, 100 and 200 milligram portions of Ca O, when 25 and 30 grams of NH₄C₂H₃O₂ was taken, the number of c.c. of (NH₄)₂Mo O₄ required was less than the number required for 250 milligrams of Pb alone. This cannot be clearly explained until more is known of the constitution of the precipitate formed.

-III -

DISCUSSION.

As was stated in the introduction, the investigation was carried on first, to clear up the apparent contradiction in the evidence of Irving Bull and the writings of Low, Furman and Pardoe, and others, and second, to find the true effect of calcium when present in the titration.

Irving Bull, in a number of experiments, carried on with Ca Cl₂ solution and a Pb (C₂H₃O₂)₂ solution found that the calcium had no effect even when there was twice as much ^{Ca. as the} lead present. In his description of the manner of carrying out the experiments he is very vague, so that no explanation as to the difference in results obtained by him can be given. It is apparent that he either converted his lead and calcium to sulphates, then dissolved them in NH₄C₂H₃O₂, etc., and then titrated or else titrated the solutions without the conversion to sulphates. Either method of procedure should have given high results, the variations being more marked and more nearly proportional by the latter method, and it is difficult to understand how he obtained results checking within less than three hundredths of a c.c. with such large amounts of calcium present.

He also carried on a number of experiments with barium present, and again his method of procedure is very vague, but it is apparent that he followed one of the two methods outlined above. In these experiments he found that the presence of barium gave low results, and when the amount of barium present was approximately equal to the amount of lead, that about 20% less $(\text{NH}_4)_2\text{MoO}_4$ was required. Here again his results vary widely from those of this investigation. As is seen from Table 5, as the barium content increases, the number of c.c.'s of $(\text{NH}_4)_2\text{MoO}_4$ required for the same amount of lead increases, and when lead and barium are present in equal amounts, about 20% excess $(\text{NH}_4)_2\text{MoO}_4$ is required.

No satisfactory explanation for this very wide discrepancy can be given, unless Bull converted his barium and lead to sulphates and in dissolving them in $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$, failed to get all his lead in solution, due to the presence of barium and ^{its} ~~the~~ retarding effect on solution (cf. Low, 5th Edition, page 148).

The statement of Löw and Furman and Pardee that insoluble calcium molybdates are formed under the conditions of titration, certainly needs modification, as is shown in the results tabulated in Table 3 and was probably made without definite experimental proof.

While this investigation does not completely solve the problem as to the exact nature of the effects observable in the lead titrations when calcium and barium are present, it does indicate very clearly to what these discrepancies are due, and suggests lines of further investigation which will clear the matter up, and no doubt substantiate the conclusions drawn herein. Due to lack of time, these investigations were not taken up, but suggestions as to their nature are given for future work.

The investigation shows that results are high when calcium or barium are present, that these are not due to an insoluble calcium or barium molybdate, but rather to some complex molybdate of calcium and lead or barium and lead. From the work done but little can be said as to the actual composition of this molybdate. Analyzation of the precipitates for Ca, Pb and Mo, would clear up this problem. This, however, presents its difficulties, as getting the precipitate away from the solution completely without changing its constitution, would be difficult. Taking a constant amount of calcium and varying the lead, and conducting the experiments in the same manner as those described for lead, with varying amounts of calcium, would also give

more information as to the constitution of the precipitate formed. The investigation also shows that this complex molybdate formed where calcium is present, is somewhat soluble in $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ and that due to this, low results might be obtained under certain conditions.

- IV -

SUMMARY.

The investigation proves the following:-

- (1) The $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$, even when present to saturation, has no solvent effect on the lead molybdate formed in the titration.
- (2) Under the conditions of titration (when no lead is present) an insoluble calcium molybdate is not formed.
- (3) When calcium or barium is present in the titration, complex calcium lead molybdates or barium lead molybdates are, ^{probably} formed which give high values. The excess of ammonium molybdate required is proportional to the amount of barium or calcium present to a maximum point, above which there is no further increase.
- (4) The calcium lead molybdates, ^{if} formed are somewhat soluble in $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$, the solubility being proportional to the concentration of the $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$. This solvent ac-

tion decreases the effect of the calcium lead molybdate and under certain conditions will even give low results.