

ON THE EFFECT OF LIME ON THE AMMONIUM MOLYBDATE METHOD OF LEAD ASSAY.*

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DURING the analytical portion of the experimental work in connection with a recent research on the "Theory of Blast Roasting of Galena" (*Bull. Inst. Min. and Met.*, 1912, No. 89), the necessity arose for ascertaining the effect of lime on the ammonium molybdate method of lead assay. On referring to published results on this point, a great divergence of opinion was found to exist, some writers stating that the presence of lime had no influence, and others that the results obtained for lead in the presence of lime were too high.

I. C. Bull (*School of Mines Quart.*, 1902, **23**, 348), who examined the effect of calcium, barium, strontium, antimony, and bismuth on the assay, came to the conclusion that calcium, bismuth, and antimony had no effect on the result, and that barium and strontium caused low results. In this work, however, Bull added the impurities to the solution of lead sulphate in a form in which they could not ordinarily exist in the course of assays, for the calcium, barium, strontium, and antimony were added as chlorides and the bismuth as nitrate.

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On following out the method as originally devised by H. H. Alexander (*Eng. and Min. J.*, 1893, **55**, 298), it is obvious that only insoluble sulphates can be left with the sulphate of lead, and also that the impurities most likely to interfere are calcium, barium, and strontium.

H. A. Guess (*Amer. Inst. Min. Eng.*, 1904, **35**, 359) points out that the molybdate method cannot be used with safety in dealing with poor lead ores containing large quantities of lime. W. H. Seamon ("A Manual for Assayers and Chemists," Chapman and Hall, 1910, p. 91) also states that the molybdate method is not reliable on low-grade ores containing much lime, and that it frequently fails when there is iron in the ores, all the sulphate of iron failing to go into solution, and obscuring the end-point with tannin. To overcome these difficulties, Seamon separates the lead by precipitation on aluminium. A. H. Low ("Technical Methods of Ore Analysis," Chapman and Hall, fifth edition, p. 152) states that Alexander's original method did not sufficiently provide for the presence of calcium, which is a frequent constituent of lead ores. Calcium forms a molybdate which is more or less insoluble under the conditions of titration, and tends to raise the results in a rather irregular manner. To overcome this, Low recommends a longer method, involving the separation of the lead from the ammonium acetate solution by means of ammonium sulphide.

In a recent paper on "Quick Combination Methods in Smelter Assays" (*Bull. Inst. Min. and Met.*, 1912, No. 89), A. F. French gives results showing that lime does not interfere with the molybdate assay as ordinarily carried out, and these results are confirmed by F. C. Robinson (*ibid.*, 1912, No. 90), who, in a written contribution to the discussion of French's paper, states that when lime is known to be present the assay, after evaporation to the point at which SO_3 fumes are liberated, is not diluted, cooled, and allowed to stand overnight, but is diluted only when it can be proceeded with at once after cooling, as calcium sulphate crystallises out and is difficult to redissolve. By washing by decantation twice with 30 c.c. of cold dilute sulphuric acid (1 per cent. by volume) and once with water, calcium sulphate is sufficiently well removed.

From the foregoing it is evident that the effect of lime on the assay is by no means clearly understood, and it is also evident that in order to correctly interpret the action of lime on the titration a solution of calcium sulphate in ammonium acetate should be used.

Preliminary experiments showed that a solution of calcium sulphate in ammonium acetate does not form an insoluble molybdate with ammonium molybdate in the absence of lead, neither does it react with the lead molybdate formed during an ordinary lead assay; for if the assay be carried out to a satisfactory end-point, and then a quantity of solution of calcium sulphate in ammonium acetate be added, the end-point is found to be permanent, no more ammonium molybdate being required to react with the lime. If, however, a solution containing sulphates of lead and lime in ammonium acetate be titrated with ammonium molybdate solution, then the lime causes a larger amount to be required, thus giving high results, the excess necessary increasing with the lime added to a certain point, after which additional lime makes no difference.

The following tables indicate the effect of the addition of increasing amounts of calcium sulphate :

TABLE I.—*Effect of Small Quantities of Calcium Sulphate on the Ammonium Molybdate Titration for Lead.*

Weight of Pb taken.	Weight of CaSO ₄ added.	c.c. Molybdate Solution required.	Lead calculated, per Cent.
0.3415 grm. ...	nil	29.0	100.0
" " ...	0.0036	29.1	100.3
" " ...	0.0073	29.2	100.7
" " ...	0.0109	29.5	101.7
" " ...	0.0146	29.8	102.7
" " ...	0.0183	29.8	102.7
" " ...	0.0256	29.8	102.7
" " ...	0.0292	29.9	103.1
" " ...	0.0327	29.9	103.1
" " ...	0.0366	30.0	103.4
" " ...	0.0402	30.2	104.1
" " ...	0.0439	30.7	105.8
" " ...	0.0475	30.7	105.8
" " ...	0.0512	30.7	105.8

On slightly altering the conditions of the experiments—as, for example, by using more dilute solutions or by varying the amounts of reagents used—the results obtained were found to vary considerably. The following table will illustrate this point; the determinations were carried out in exactly the same manner as the previous set, but a smaller quantity of lead was taken.

TABLE II.—*Effect of Larger Quantities of CaSO₄ on the Ammonium Molybdate Titration for Lead.*

Weight of Pb taken.	Weight of CaSO ₄ added.	c.c. Molybdate Solution required.	Lead calculated, per Cent.
0.2005 grm. ...	nil	18.7	100.0
" " ...	0.0549	19.4	103.7
" " ...	0.0612	19.6	104.8
" " ...	0.0658	19.6	104.8
" " ...	0.0695	19.6	104.8
" " ...	0.0732	19.6	104.8
" " ...	0.0805	19.6	104.8
" " ...	0.0842	19.7	105.3
" " ...	0.0915	19.7	105.3
" " ...	0.0951	19.8	105.9
" " ...	0.1134	19.9	106.4
" " ...	0.1317	19.9	106.4
" " ...	0.1500	20.0	106.9
" " ...	0.1685	20.0	106.9
" " ...	0.1866	20.0	106.9
" " ...	0.2049	20.2	108.0
" " ...	0.2232	20.2	108.0
" " ...	0.2415	20.4	109.1

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It will be seen, on comparing these tables, that mass action plays a considerable part in these reactions; for in the case of Table II., in which the lead solution is more dilute, 0.0915 grm. calcium sulphate (45.6 per cent.) interferes to a less extent than 0.0512 grm. calcium sulphate (15 per cent.) does in the results given in Table I.

The table given below shows the effect of larger quantities of calcium sulphate on the assay. In this case separate weights of the sulphate and of the calcium sulphate were taken, the same amount of ammonium acetate was used in each case, and the whole conditions of the experiment were kept identical.

TABLE III.

Weight of Pb taken.	CaSO ₄ taken. Grms.	CaSO ₄ per Cent. of PbSO ₄ present.	c.c. Ammonium Molybdate required.	Lead calculated, per Cent.
0.25 grm. ...	—	—	23.7	100.0
" " ...	0.055	15	25.1	105.9
" " ...	0.110	30	26.1	110.1
" " ...	0.183	50	26.7	112.6
" " ...	0.256	70	27.1	114.3
" " ...	0.329	90	27.1	114.3
" " ...	0.366	100	27.1	114.3
" " ...	0.549	150	27.1	114.3

From the results given it will be seen that calcium sulphate, even in small quantities, causes high results to be obtained for lead; but from Table III. it will also be seen that the range of this interference is limited to a certain amount, above which no further increase in the lead results is obtained.

When the conditions of the experiments are not kept absolutely constant, the presence of calcium sulphate raises the results in an irregular manner, as stated by Low (*loc. cit.*); but when the conditions are kept the same, then additions of calcium sulphate cause systematic increases in the calculated amount of lead present. There are indications that double molybdates are precipitated when calcium sulphate is present; for on calculating from the molybdate used the composition of the precipitate formed in the case of the results given in Table III., the following results are found:

CaSO ₄ present.				Calculated Formula of Precipitate.		
15 per cent. of the PbSO ₄ present.				17 PbMoO ₄ , CaMoO ₄ .		
30	"	"	"	10	"	"
50	"	"	"	8	"	"
70 to 150	"	"	"	7	"	"

The results of similar experiments in which a solution of lime in ammonium acetate was used in place of the calcium sulphate solution are given in Table IV., and in this case a more dilute solution of ammonium molybdate was used, to insure greater accuracy, the first 100 c.c. in each case being added by means of a Stas pipette.

TABLE IV.—*Effect of Lime on the Ammonium Molybdate Titration for Lead.*

Weight of Pb taken.	CaO added. Grms.	CaO per Cent. of PbSO ₄ present.	c.c. Ammonium Molybdate required.	Lead calculated, per Cent.
0.3074 grm. ...	—	—	106.5	100.0
" " ...	0.0225	5	108.3	101.7
" " ...	0.0450	10	109.1	102.4
" " ...	0.0675	15	109.9	103.2
" " ...	0.0900	20	110.7	103.9
" " ...	0.1350	30	111.8	105.0
" " ...	0.2250	50	113.0	106.1
" " ...	0.4500	100	114.6	107.6
" " ...	0.6750	150	115.4	108.3

From these figures it is seen that lime acts in a similar manner to calcium sulphate in causing high results to be obtained for lead when the lime is present in the ammonium acetate solution of the lead sulphate. On carrying out a large number of experiments with lime, under somewhat varying conditions as to strength of solution, etc., the same irregularities as to the amount of interference introduced were noticed.

Similar experiments carried out with barium and strontium sulphates show that these act in quite a different manner; for by boiling mixtures of these sulphates with sulphate of lead in ammonium acetate solution somewhat low results were obtained in every case, owing to these insoluble sulphates holding small quantities of lead sulphate, and thus preventing the complete solution of the lead.

From this work the following conclusions may be drawn: (1) That lime or calcium sulphate in solution in ammonium acetate does not form an insoluble molybdate when boiled with ammonium molybdate solution. (2) That lime or calcium sulphate in ammonium acetate solution does not react with precipitated lead molybdate. (3) That when lime or calcium sulphate is present with lead sulphate in ammonium acetate solution, then, on boiling with ammonium molybdate solution, the insoluble molybdate formed contains both lead and lime. (4) From conclusion (3) it follows that it is impossible to determine lead sulphate direct by solution in ammonium acetate when lime or calcium sulphate is present; and (5) in the ordinary lead assay for materials containing lime, etc., it is necessary to separate the lead, or else to take special precautions to wash the lead sulphate free from calcium sulphate before proceeding with the solution of the lead sulphate. (6) Barium and strontium sulphates do not act in the same manner as calcium sulphate, and tend to give low results instead of high results.

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DISCUSSION.

Mr. RICHMOND asked whether the authors had any further data as to the composition of these double molybdates beyond the excess of molybdate used. Had the double molybdate been actually separated, and its composition determined? Looking at the figures, it seemed to him that by no means all the calcium had been precipitated, and that the proportion that was precipitated was not the same in every case. He should like also to ask whether the authors could give the reason why there was no further increase in the percentage of lead found when the calcium sulphate exceeded 70 per cent. Was it due to the fact that the solution was saturated, and that the excess of calcium sulphate was not in solution? Or was it due to the fact that under the conditions of mass action an equilibrium was approached at the point where the maximum figure was obtained?

Mr. RAYMOND ROSS asked whether any of the impurities referred to were likely to be found in the finished lead—*i.e.*, in ordinary commercial lead.

Mr. BANNISTER, in reply, said that the actual composition of the double molybdates had not been ascertained; it would be seen from the paper that the readings obtained were merely considered to be an indication that double molybdates were formed. It was, however, curious that the results of a whole set of experiments should calculate out almost exactly in molecular proportions. They could not explain why the increase in the figures for lead stopped when 70 per cent. of calcium sulphate was reached. The saturation-point, however, was certainly not reached there, for even with as much as 150 per cent. of calcium sulphate the whole of this went into solution before the titration was commenced. These impurities were present in many lead ores, and also in lead slags and other furnace products, and it was important that the possibility of interference should be recognised in commercial work.

