CIX.—*A Method for the Volumetric Estimation of Lead.*

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VERY numerous methods have been proposed for the volumetric estimation of lead, but in many instances their use remains limited to the determination of lead in a simple solution of a salt, and they are, therefore, not available for lead sulphate, in which form lead is very usually separated from other metals.

The methods of titration in use are both direct and indirect. Few compounds of lead exist which can be quantitatively precipitated by a solution of a soluble salt, for a slight excess of which a suitable indicator is available. On this account, the direct methods of titration are small in number. The titration by means of a solution of ammonium molybdate, devised by Schindler (*Zeitsch. anal. Chem.*, 1888, **27**, 137), and adapted by Alexander to the analysis of ores (*Engin. and Min. Journ.*, **55**; A., 1893, ii, 599), and Beebe's ferrocyanide method (*Chem. News*, 1896, **73**, 18), are the best known examples of the direct methods. The first has the advantage of being applicable to solutions of lead sulphate in such solvents as sodium acetate, but is, in any case, of only moderate accuracy, on account of the unsatisfactory behaviour of tannin as an indicator for a soluble molybdate. The second method can only be used for lead in a solution slightly acid with acetic acid, although under these conditions the use of a uranium salt as indicator allows the end-point to be fixed with fair exactness.

Other direct methods have received consideration, but by far the greater number, descriptions of which are found in the literature, are indirect in application. The dichromate method is probably the best known example. It may be applied in several ways; the chromic acid in either the lead chromate precipitate or in the potassium dichromate added in excess of that required to effect this precipitation may be determined. A very convenient procedure is to cause the excess of dichromate to liberate iodine from potassium iodide, and, to titrate the iodine with starch. This modification is commended by Longi and Bonavia (*Zeitsch. anorg. Chem.*, 1898, **17**, 158) in a very extensive report on the available methods for lead estimation. In spite of some uncertainty regarding the constitution of lead chromate produced by precipitation from solutions of lead sulphate in such media as slightly acid sodium acetate, the indirect chromate method remains probably

the best of its class (see also Low, "Technical Method of Ore Analysis," 1911, p. 144).

It is, nevertheless, evident that the volumetric determination of lead does not rest altogether on a satisfactory basis. It is remarkable that the literature dealing only with the few typical methods mentioned is very extensive, and that in it notices of criticism and modification of methods are very common (see Weber, *Zeitsch. anal. Chem.*, 1903, **42**, 628, for a general report).

It is evident that there is still a need for a method which is at once fairly accurate and rapid, is immediately applicable to lead sulphate, and is subject to as little disturbance as possible by the presence of such other sulphates as cannot easily be separated from that of lead.

Attempts were accordingly made to liberate the sulphuric acid from lead sulphate, and to estimate the lead by titrating the liberated acid. Experiment proved that the quantitative conversion of lead sulphate into sulphide could readily be carried out, and indicated that the estimation of lead depending on it was likely to bear comparison, in point of accuracy and of time required, with any other volumetric method. It is also an advantage that the procedure depends on a thoroughly known and definite reaction.

The method proposed is, of course, a perfectly general one, although its application to lead sulphate does not seem to have been worked out. Other methods involving acidimetry, however, have been devised. Ruoss (*Zeitsch. anal. Chem.*, 1898, **37**, 427) proposed to make use of the reaction between lead sulphate and baryta in boiling solution, by which a basic salt of the composition $\text{PbSO}_4 \cdot \text{PbO}$ and barium sulphate were said to be formed. His method consisted in precipitating the sulphate from a neutral solution of lead by means of excess of sodium sulphate, boiling, and titrating the liquid holding the lead sulphate in suspension, with baryta-water. Only one numerical result is given; the suitability of the procedure to deal with lead sulphate produced by evaporation with sulphuric acid, and the error introduced by the initial presence of metals other than lead, are not discussed.

Koenig's method (Bull, *Zeitsch. anal. Chem.*, 1902, **41**, 653) entails the conversion of the sulphate into carbonate by digestion with a solution of ammonium carbonate, washing the carbonate free from water, and dissolving it in a measured volume of standard dilute nitric acid. By titration with standard alkali, after methyl-orange has been added, the excess of acid—and, indirectly, the amount of lead—can be determined. This method is reported on favourably by Bull, who used it in the assay of lead ores, and also

investigated the effect of other metals in admixture with the lead. Barium and calcium were naturally found to cause high results. Bismuth and antimony were apparently without effect, although it is to be noted that in no case was a salt of any of these metals added to the lead solution previous to evaporation with sulphuric acid, and that, as will be seen later, the main cause of the adsorption of metallic salts by the lead sulphate, which occurs during the ordinary procedure, was absent.

In the experiments made to test the method discussed in the present paper, quantities of lead sulphate were prepared as required, by evaporating with sulphuric acid, until the acid was vaporising freely, known volumes of a solution of pure lead nitrate containing almost exactly 0.0200 gram of lead per c.c. Preliminary experiments were made with lead sulphate, prepared by adding excess of sulphuric acid to the lead nitrate solution, filtering, and washing with water. It was found that this substance reacted completely with a saturated aqueous solution of hydrogen sulphide at a temperature of about 30° , but that the sulphate produced by the drastic evaporation with sulphuric acid was far more difficult to convert.

In view of the considerable solubility of lead sulphate in hot sulphuric acid, it seemed likely that the evaporation and subsequent cooling would result in the deposition of at least some of the salt in a comparatively dense form. A microscopic examination proved this to be the case, and made clear the difference in behaviour of the two forms. Lead sulphate which has been precipitated from a dilute solution by adding concentrated sulphuric acid and filtering, consists of a clot of minute, prismatic needles (Fig. 1). When this substance is boiled with sulphuric acid, it is completely changed in appearance; the minute needles give place to much denser, branched, skeletal growths, the branches of which are here and there terminated by prism faces. A few four- and eight-sided orthorhombic prisms are also to be seen; these have evidently crystallised out while the acid was cooling (Fig. 2).

After further experiment, the following procedure was found to be most convenient, and was adopted, with only unessential modifications, for all experiments performed to test the method, and, later, for all lead assays made by it. The mixture of lead sulphate and sulphuric acid, produced by evaporation (preferably in a conical Jena-glass flask) to the point at which white fumes are evolved, is cooled, and 50 c.c. of water are added. After the contents of the flask have attained the ordinary temperature, the lead sulphate is transferred to a 7 cm. filter paper, any washing which is necessary to remove soluble sulphates being done with 5 per cent. sulphuric

× 300.

FIG. 2. (See p. 990.)

× 300.

FIG. 3. (See p. 998.)

× 300.

[To face page 990.]

acid. The free acid is then removed by washing four times with a mixture of equal volumes of alcohol and water, care being taken to direct the jet of liquid under the fold of the paper.

The washed sulphate is then transferred, with the paper, to a conical Jena-glass flask of 300 c.c. capacity. A freshly prepared, saturated aqueous solution of hydrogen sulphide, to the extent of 10 c.c. for each tenth of a gram of lead present, is added; the upper part of the flask is heated by a Bunsen flame to expand slightly the enclosed air, and a red-rubber stopper of good quality is inserted and forced home. The flask and its contents are then shaken vigorously to disintegrate the filter paper, and are heated over the free flame until they are as hot as the hand can conveniently bear. They are allowed to remain for at least twenty minutes, the temperature being kept at about 50° by occasional heating. Each heating is accompanied by energetic shaking.

After being cooled under the tap, or in a suitably designed flask-cooler, the flask is shaken so that the hydrogen sulphide may be partly reabsorbed by the cold liquid, the stopper is carefully removed, and the adhering liquid washed into the flask. If the precautions mentioned are not taken in order to establish a negative pressure in the flask before it is opened, serious error may result by liquid being blown out when the stopper is withdrawn. There should be a marked odour of hydrogen sulphide when the flask is opened; if none can be perceived, the experiment should be rejected. In no case should the flask be allowed to stand overnight before opening, for in many instances in which delay had occurred, an odour of mercaptan was noticed whenever alcohol had been used to wash the sulphate, and the sulphuric acid liberated was less than the calculated amount.

The acid liquid is most readily filtered from the lead sulphide and disintegrated paper on a filter of paper pulp. A convenient arrangement, when many estimations are being made, is to have a funnel inserted in one hole of a cork fitting the conical flasks of the size mentioned above, and a leading tube, connected to a filter pump, fitted into the other hole. A fragment of filter paper is moistened, loosely crumpled into a ball about 1 cm. in diameter, and allowed to fall into the apex of the funnel. Filter pulp, made by shaking a 9 cm. paper in 200 c.c. of water, is then run in, and slight suction applied. Through such a filter the acid liquid can be run very quickly. The flask is washed out twice with distilled water, and the washings also filtered; finally, the material is pressed down with the end of the finger to facilitate the removal of most of the liquid. For preparing the filter, performing the filtration, and washing, in any usual case, five minutes are amply sufficient.

The filtrate is boiled for two minutes to remove hydrogen sulphide, cooled, and titrated with $N/10$ - or $N/5$ -sodium hydroxide, methyl-red being used as indicator.

Two modifications of the method are sometimes useful. The first is to collect the lead sulphate on a Gooch crucible, either paper pulp or asbestos being employed to line the bottom of the crucible. By this means, the time required for washing with the alcohol-water mixture is reduced, but the removal of the precipitate from the crucible to the flask is more difficult than by the method already described, and the results, as the figures given in the first table indicate, were never found to be so trustworthy. In this connexion, it may be mentioned that the filter paper seems to be a necessity to the complete decomposition of the lead sulphate by the hydrogen sulphide. It was found that lead sulphate filtered on asbestos in a Gooch crucible never gave the expected quantity of sulphuric acid in the next stage of the process. When a piece of filter paper had been added, however, the results were normal. It is probable that the larger crystals of the sulphate tend to become coated with sulphide, which is removed by the abrading action of the paper pulp.

The second modification of the process was found to be of considerable value in cases where the lead sulphate is necessarily mixed with a large amount of finely divided, insoluble matter. In such an instance as that of the mixtures of lead and calcium sulphates discussed below, the washing with aqueous alcohol proves to be extremely tedious. Here it is advantageous to transfer the filter paper and precipitate to the decomposition flask as soon as the washing with dilute sulphuric acid is over, and to disintegrate the paper thoroughly by shaking it with a little water, the usual precautions being taken on closing and opening the flask. A few drops of methyl-red solution are then added, and the mixture is neutralised with $N/5$ -sodium hydroxide. In estimations made in this way (method B), the acid in the final filtrate is always higher than would be the case if the usual washing (method A) were performed. The error is a fairly constant one, however; it amounts usually to 1 in 250, and may be eliminated from an estimation by suitable standardisation of the alkali. It is probably due to adsorption by the paper of a small amount of sulphuric acid which is removed by the subsequent washing.

The results of a series of experiments made to test the method are given in the table below. In each case, 3 c.c. of sulphuric acid were used in the evaporation. Pure assay lead was employed in three instances, but in all others the appropriate volume of lead nitrate solution was measured out with a pipette. The lead

present in each solution used was determined by gravimetric estimation as sulphate.

In order to secure that the lead sulphate produced from a given volume of lead solution should be the same in the gravimetric and volumetric estimation, the lead sulphate was prepared and washed, so far as possible, in the same way in both estimations. In the former case, however, Gooch crucibles were used, and the sulphate was dried for one hour at 150° before weighing. In the instance of the first two solutions prepared:

19.96 c.c. gave 0.5832 PbSO_4 containing 0.3985 Pb.

19.96 " " 0.6054 " " 0.4137 "

TABLE I.

Sodium Hydroxide Solution.

0.9582 $N/10$, 1 c.c. equivalent to 0.009925 gram of lead.

0.9840 $N/5$ " " " 0.002038 " "

Method.	Lead solution used. c.c.	Sodium hydroxide required. c.c.	Lead found gravimetrically.	Lead found volumetrically.
A. {	19.96	40.07($N/10$)	0.3985	0.3977
	"	40.02 "	"	0.3972
	"	40.16 "	"	0.3985
	"	40.12 "	"	0.3981
	"	41.56 "	0.4137	0.4124
	"	41.58 "	"	0.4127
	29.96	29.26($N/5$)	0.5982	0.5964
	"	29.32 "	"	0.5976
	"	40.82($N/10$)	0.4065	0.4050
	"	47.85 "	0.4757	0.4749
	"	55.38 "	0.5490	0.5495
	19.96	40.00 "	0.3985	0.3970
B. {	"	40.05 "	"	0.3975
	"	39.98 "	"	0.3969
	"	40.22 "	"	0.3991
	25.05	24.68($N/5$)	0.5000	0.5028
	"	24.64 "	"	0.5021
	"	24.60 "	"	0.5013

From the first series of figures, comprising the results of eleven experiments in which the lead sulphate was collected and washed by method A, it will be seen that the mean amount of lead found by the indirect titration, calculating from the normality of the sodium hydroxide solution, is less than that found gravimetrically or originally weighed out, by about 0.20 per cent. In a volumetric estimation, this error is satisfactorily small, and may, in any case, be eliminated by standardising the alkali with reference to weighed amounts of lead. In none of the series of eleven experiments does the result fall below the mean of all the results by more than 0.20 per cent.

It is therefore clear that if the preliminary isolation of pure lead sulphate can be performed, the accuracy of the proposed method of estimation is as high as the accuracy with which a volumetric process can generally be conducted without special precautions. Nor is the procedure expensive of time; a single estimation can be carried out, exclusive of weighings, in from an hour and a-half to two hours, and three or four worked together require very little longer.

The whole of the operations involved are most readily carried out in conical flasks of Jena-glass. Boiling and evaporation can be done most rapidly by manipulating the flasks over a Bunsen flame working at full power. The liquid in the flask is given a swirling motion with the hand, so that even if spirting takes place, nothing is lost through the mouth. Preliminary experiments were made to test this method of evaporation, but in no case was any detectable error found to accompany the evaporation to complete dryness of 75 c.c. of liquid.

For the manipulation of the flasks, an efficient flask-holder,

FIG. 4.

which is manageable entirely by one hand, and does not cramp the fingers, is absolutely necessary. No such article being readily obtainable, the holder represented in Fig. 4 (actual length, 18 cm.) was made up from iron strip 0.8 cm. wide. Pieces of cork shaped to fit the necks of the flasks are fitted into the ends of the holder; they are easily renewed. The holder is grasped with the hand so that the fingers are inserted into the looped end. In this way a broad grip is combined with complete freedom to open and close the jaws of the instrument.

THE ESTIMATION OF LEAD IN PRESENCE OF OTHER METALS.

The indirect acidimetric method described in the present paper is evidently sufficient for the estimation of lead in every case in which lead sulphate can be obtained, and lead is the only metal present. More generally, lead is accompanied by other metals. When a complex substance containing lead is dissolved in hydrochloric or nitric acid, and evaporation with sulphuric acid is

employed in order to remove the acids which would increase the solubility of the lead sulphate, two causes of complication may be present. The lead sulphate may be precipitated with the sulphates of the alkaline earth, or may carry down from solution certain salts, otherwise soluble, which cannot be removed by subsequent washing. It was necessary to ascertain the effect of these occurrences on the accuracy of the proposed method.

The information on this subject, which is available in the literature, was found to be sparse and uncertain. There is general agreement in one case, however. It is acknowledged that the complete separation of lead from antimony or tin, by precipitation as sulphate, is impossible, although, by the addition of a tartrate, contamination of the lead sulphate by antimony compounds can in some measure be prevented (Low, *Chem. News*, 1893, **67**, 178). In the case in which either of these metals is present, or in which both are present together, the separation is preferably made in some other way, often conveniently by means of their sulphides (Blakely and Chance, *J. Soc. Chem. Ind.*, 1911, **30**, 518). The cases of antimony and tin will therefore not be discussed. Among other metals important in this connexion, it was thought that interference might be expected from calcium, barium, copper, iron, and bismuth. The influence of each five metals was investigated.

The method adopted was to make up a solution of a salt of each of the metals in question, and if a definite weight of salt could not be weighed out for this purpose, to estimate the weight of metallic element in a known volume of each solution. In each experiment, a measured volume of such a solution was mixed with a measured volume of lead solution, 5 c.c. of sulphuric acid were added, the mixture was evaporated, cooled, and diluted with 50 c.c. of water. The diluted liquid was boiled for two minutes, and then cooled. The amount of lead sulphate which contains 0.4 gram of lead was found most convenient to manipulate; the volume of solution corresponding nearly with this weight of lead was accordingly used in each experiment.

In stating the results, the weight of lead present, as inferred from a gravimetric analysis of the lead solution used, has always been given. The lead estimated by titration has been calculated, where method A was used, from the normality of the decinormal alkali; where method B was preferred—in the cases where calcium and barium were present—the amount of lead to which 1 c.c. of alkali was practically equivalent, was obtained from the mean of the last three results of table I, and this figure was used instead of that deduced from the normality of the alkali.

Estimation in Presence of Calcium.

The mixture of lead and calcium sulphates filters rather slowly, and, when a large amount of calcium is present, requires a very long time to wash. By the use of a Gooch crucible, or by substituting neutralisation of the precipitate for washing it (method B), or by both these means together, the work can be done much more rapidly. A solution of calcium chloride, made by dissolving calcite in hydrochloric acid, and containing 0.01 gram of calcium in 1 c.c., was used. The results are given in table II.

TABLE II.

Sodium Hydroxide Solution, 1 c.c. equivalent to (A), 0.009925 gram of lead; (B), 0.009881 gram of lead.

Means of filtration.	Method.	Ca present.	Sodium hydroxide required. c.c.	Lead found volumetrically.	Lead found gravimetrically.
Paper	A	0.05 gram	41.30	0.4099	0.4096
"	B	0.10 "	40.36	0.3988	0.3985
"	"	0.20 "	40.32	0.3985	"
Gooch	A	0.40 "	39.94	0.3964	"
"	"	" "	39.92	0.3962	"
Paper	B	" "	41.50	0.4101	0.4096

The results of the tests in which a Gooch crucible was used are, as usual, slightly low, but it is evident that the presence of even 0.4 gram of calcium introduces no considerable error. Such a mixture is an extreme instance, and would be represented in a practical case by a galena ore containing 72 per cent. of calcite.

Estimation in Presence of Barium.

The introduction of even 0.02 gram of barium was found to cause the conversion of lead sulphate to the sulphide to be incomplete, and extension of the time of digestion with hydrogen sulphide was not found to make it appreciably more complete. The first four results in table III were obtained by the ordinary procedure.

It has occasionally been noticed that the presence of barium sulphate renders difficult the solution of lead sulphate in sodium or ammonium acetate, when both sulphates have been heated with concentrated sulphuric acid. Bannister and McNamara (*Analyst*, 1912, **37**, 242) found that the molybdate titration of lead gave low results when barium or strontium was present, and the separation of lead in this way was attempted. Low recommends that the sulphates obtained in the assay of lead ores containing barium

should be extracted with boiling hydrochloric acid to dissolve the lead (Low, "Technical Methods of Ore Analysis," 1911, p. 148).

In the present case, sodium hydroxide is the most suitable solvent. By the following method of dissolving and reprecipitating the lead sulphate, normal results can be obtained in cases where the barium does not exceed 25 per cent. of the lead; with a higher proportion of barium, no practicable method of rendering all the lead sulphate open to decomposition by the hydrogen sulphide could be found.

The preliminary evaporation is continued until no liquid sulphuric acid remains in the flask. After cooling, 10 c.c. of water are added, followed by 10 c.c. of a 30 per cent. solution of sodium hydroxide. The alkaline solution is kept near its boiling point for about five minutes, with occasional shaking, and, after cooling, the lead sulphate is recovered by the addition of 50 c.c. of 20 per cent. sulphuric acid. The liquid is cooled, and the sulphate collected as usual. Method B is preferable, on account of the fine state of division of the precipitate.

The results of tests are given in table III. All precipitates were collected on 7 cm. filter papers, as usual. The lead equivalents, in methods A and B, of the *N*/10-alkali are the same here as in table II. A solution of barium chloride containing 0.01 gram of barium per c.c. was employed.

TABLE III.

	Method.	Ba present.	Sodium hydroxide used. c.c.	Lead found volumetrically.	Lead found gravimetrically.
Ordinary Method ...	A	0.02 gram	38.30	0.3801	0.3985
	B	0.20 "	29.90	0.2955	"
	"	" "	32.75	0.3236	"
	"	" "	29.80	0.2945	"
Double precipitation	B	0.02 gram	40.47	0.3998	0.3985
	"	0.05 "	40.22	0.3975	"
	"	" "	40.33	0.3985	"
	"	0.10 "	40.25	0.3977	"
	"	0.20 "	39.92	0.3945	"
	"	" "	39.92	0.3945	"
	"	" "	39.67	0.3920	"

It is evident that the method of double precipitation is necessary even when barium equal to only 5 per cent. of the lead is present, but that it is insufficient to secure accurate results when more than five times this quantity of barium has to be dealt with. Natural barytes, being freely soluble in hot sulphuric acid, is just as much a cause of error as the barium sulphate produced in these tests.

In order to ascertain the cause of this interference, a mixture of lead and barium sulphates, in which the relation between the weight of the lead and that of the barium was as two to one, was prepared by the ordinary method of evaporation with sulphuric acid and subsequent addition of water, and was then washed with alcohol, dried, and examined under the microscope. In order to distinguish between crystals of the two sulphates by Becke's method, the precipitate was immersed in methylene iodide, the refractive index of which is intermediate between the mean refractive indices of the two substances in question. An oil-immersion lens of 2 mm. focus was employed. By these means, the precipitate can be seen to consist of minute prisms of lead sulphate, clusters of which are cemented together by a matted mass of indistinctly crystalline barytes (Fig. 3). Here and there the barium sulphate completely encloses the prisms. The whole forms a confused mass, with no appearance of parallel growth of the two sulphates.

The solubility of barium sulphate in hot sulphuric acid is much greater than that of the corresponding lead compound, and it has much less tendency to crystallise from the cooled solution than the lead sulphate, although in any case such a crystallisation results in deposition of barium hydrogen sulphate, which is immediately decomposed by water. It is evident from these facts (Liès-Bodart and Jacquemin, *Compt. rend.*, 1858, **46**, 1207) and from the microscopic appearance of the mixed precipitate, that the addition of water causes all the barium salt very rapidly to crystallise out and partly to enclose the lead sulphate which is simultaneously being precipitated, as well as that which has crystallised previously.

Estimation in Presence of Copper.

The introduction of copper was not found to cause sensible error. The tests were made by method A. No special precautions were found necessary. The boiling after the addition of the 50 c.c. of water must, of course, not be omitted. A solution of copper sulphate, containing 0.02 gram of copper in 1 c.c., was made by dissolving electrolytic copper foil in nitric acid and evaporating with sulphuric acid. Table IV contains the results.

TABLE IV.

1 c.c. *Sodium Hydroxide equivalent to 0.01082 gram of lead.*

(Method A.)

Cu present.	Sodium hydroxide used. c.c.	Lead found volumetrically.	Lead found gravimetrically.
0.1 gram	36.73	0.3975	0.3985
0.2 "	38.15	0.4128	0.4137
" "	38.20	0.4134	"
0.4 "	38.17	0.4131	"
" "	38.25	0.4139	"
0.8 "	38.24	0.4138	"
" "	38.10	0.4123	"

Estimation in Presence of Iron.

Very many tests were made in which solutions containing lead and iron were evaporated with sulphuric acid. The conditions were varied as widely as possible, but the lead sulphate was invariably contaminated with a ferric salt, which could not be removed by washing. In every case in which a salt of iron had been initially added, no matter what subsequent procedure was adopted, the liquid from which the lead sulphide had been filtered off was found to contain more or less ferrous sulphate, produced by the reducing action of hydrogen sulphide on the ferric salt attached to the lead sulphate. In all such cases, the end-point of the titration, as indicated by methyl-red, was slightly indefinite, and the volume of alkali required was abnormally high.

The colour of the lead sulphate was found to be no indication of its purity. When small amounts of iron were present previous to the evaporation, the titration was not found to be seriously in error, but the colour of the residue was frequently pale lemon-yellow or brown. Larger amounts of iron were observed to cause very considerable error, yet the residue had very often no perceptible tinge of colour.

Once the ferric salt has become attached to the lead sulphate, washing is powerless to remove it. Varying statements are to be found in the literature regarding the time which should be devoted, after the expulsion of volatile acids by sulphuric acid and the subsequent dilution with water, to heating the solution in order to secure solution of all ferric sulphate. In the course of these tests, it was found that all soluble ferric salt dissolved almost at once on boiling; heating for more than two minutes longer is useless. The experiments, of which the results are given in table V, were made, as usual, in this way, with the exception of that

marked (a), in which instance boiling was continued for half an hour, with frequent agitation, and those marked (b) and (c), in which the sulphate was washed free from the acid liquid which contained most of the iron, and boiled three times with successive quantities of 25 c.c. of 5 per cent. hydrochloric acid. It is evident that neither procedure is of any use.

Varying the amount of sulphuric acid used for the evaporation had no effect. The contamination was found to be less when hydrochloric acid was added than when sulphuric acid was used alone; the presence of nitric acid was found slightly to increase it. A series of tests was accordingly made, in each of which the nitric acid in the usual volume of the lead nitrate solution was destroyed by repeated evaporation with hydrochloric acid. A measured volume of a standardised solution of ferric chloride was then added in each case, followed by 15 c.c. of concentrated hydrochloric and 5 c.c. of concentrated sulphuric acid. Evaporation, filtration, and washing were carried out as usual. The results of the subsequent titrations are given in the lower section of table V; those in the upper section were made with ferric sulphate.

TABLE V.

1 c.c. *Sodium Hydroxide equivalent to (Method A) 0.009925 gram of lead.*

Iron used.	Sodium hydroxide used. c.c.	Lead (apparent) found by titration.	Lead found gravimetrically.
0.075 gram (as sulphate)	40.18	0.3988	0.3942
0.15(b) " "	40.13	0.3983	"
0.45(c) " "	40.43	0.4013	"
0.075 " (as chloride)	39.87	0.3957	"
" " "	39.90	0.3960	"
0.15 " "	39.90	0.3960	"
0.30 " "	40.15	0.3985	"
0.45(a) " "	40.18	0.3988	"
" " "	40.20	0.3990	"

Even when such favourable conditions hold as those under which the second series of results in table V was obtained, the presence of 0.4 gram of iron is the source of an error of 1.2 per cent. The error is sometimes much greater; abnormally large amounts of iron are occasionally carried down for no apparent reason.

It was ascertained, after trying many expedients, that the iron could be almost entirely removed by dissolving the lead sulphate in hydrochloric acid and evaporating again with sulphuric acid. After the acid remaining from the first evaporation has been diluted and cooled, the liquid is filtered off, as much of the precipitate as possible being kept in the flask. The residue is then

washed with 5 per cent. sulphuric acid, and dissolved by heating with a mixture of 15 c.c. concentrated hydrochloric acid and 10 c.c. of water; 5 c.c. of concentrated sulphuric acid are added, and the evaporation and dilution performed as before.

The solution finally titrated in tests made in this way contained only traces of iron. On the other hand, unless care is taken to cool the liquid before each filtration, some loss of lead sulphate may occur. The results are given in Table VI. Percentage errors are given in the last column but one, and in the last the corresponding figures for the tests of table V.

TABLE VI,
(Method A.)

Iron added.	Sodium hydroxide used. c.c.	Lead (apparent) found by titration.	Lead found gravimetrically.	Error per cent.	Error from Table V.
0.075 gram	41.37	0.4105	0.4096	+0.22	+0.37
					+0.45
0.15 "	41.29	0.4097		+0.02	+0.45
" "	39.82	0.3952	0.3942	+0.25	
0.30 "	39.62	0.3932	"	-0.25	+1.07
" "	39.87	0.3957	"	+0.37	
0.45 "	39.70	0.3940	"	-0.05	+1.15
" "	41.28	0.4096	0.4096	0.00	+1.20
" "	41.23	0.4091	"	-0.12	
0.60 "	39.64	0.3934	0.3942	-0.20	
" "	39.70	0.3940	"	-0.05	
0.90 "	41.50	0.4118	0.4096	+0.55	
1.20 "	41.45	0.4113	"	+0.42	

Estimation in Presence of Bismuth.

The results given in table VII show that the lead sulphate carries down sufficient bismuth sulphate under the usual conditions to render the results invalid. Solution of all bismuth is not to be effected by boiling the diluted acid liquid. In the test marked (a), the liquid was kept gently boiling for half an hour.

The tendency to the deposition of basic bismuth sulphate was met by increasing the volume of sulphuric acid added to 10 c.c.; a series of tests made with bismuth, but with no lead, showed that with this amount of acid no basic sulphate should be formed on dilution under the usual conditions, unless the bismuth present amounted to 0.6 gram. Nevertheless, 0.02 gram introduces a serious error. The interference can hardly be due to hydrolysis of the bismuth sulphate, and is more probably due to deposition of the two sulphates from the concentrated acid solution, during cooling, in such a form that the bismuth cannot be dissolved out. Bismuth sulphate has a marked solubility in hot sulphuric acid.

TABLE VII.

(Method A.)

1 c.c. *Sodium Hydroxide equivalent to 0.01082 gram of lead.*

Bismuth added.	Sodium hydroxide used. c.c.	Lead (apparent) found by titration.	Lead found gravimetrically.	Error per cent.
0.02 gram	38.60	0.4177	0.4137	+1.0
0.05 "	38.53	0.4170	"	+0.8
0.10 "	38.70	0.4187	"	+1.25
0.20 "	38.80	0.4197	"	+1.5
0.20(a) "	38.70	0.4187	"	+1.25
0.30 "	38.51	0.4168	"	+0.80

From the results of this series of experiments, it is quite clear that the separation of lead from other metals as sulphate, by evaporation with sulphuric acid, is very liable to be incomplete. The solubility in the concentrated acid of the sulphate of the added metal is certainly the cause of the interference in the case of barium and probably also in that of bismuth. Ferric sulphate, on the other hand, has no perceptible solubility in hot sulphuric acid, and the adhesion of this salt seems to occur before the acid has become concentrated.

Partly on account of the high atomic weight of lead, the accuracy of the present method is more affected by the adhesion of salts which react with hydrogen sulphide than is the gravimetric method. In the gravimetric estimation of lead in such mixtures as have been considered, the contamination of the lead sulphate would, however, be considerable in many cases, and is probably often overlooked. For instance, the volumetric estimation of lead in a mixture of this metal with an equal weight of iron has been seen to be in error by about 1.20 per cent. Assuming that the adhering salt is normal ferric sulphate, this corresponds with 0.52 per cent. of impurity in the lead sulphate, or to 0.21 per cent. if the precipitate is heated to such a temperature that ferric oxide is the only remaining compound of iron.

THE ESTIMATION OF LEAD IN ORES.

In order thoroughly to test the method, the estimation of lead in a number of specimens of galena in association with other minerals was undertaken, and the results were compared with those obtained by the gravimetric method.

A solution of sodium hydroxide was first standardised. This is best carried out by treating a weighed quantity of pure assay lead foil with 5 c.c. of concentrated sulphuric acid, and boiling until no free sulphur is to be seen inside the flask, then cooling, and

diluting as usual. The solution of sodium hydroxide was 0.1046*N*; the calculated lead equivalent was therefore 0.01082 gram per c.c. The results are given below:

Method.	Weight of lead taken.	Sodium hydroxide used. c.c.	Lead value of sodium hydroxide solution.
A.	0.4080	37.62	0.01085
	0.4280	39.40	0.01087
	0.4295	39.60	0.01085
B.	0.4300	39.76	0.01081
	0.3647	33.73	0.01081

For the volumetric estimation, the finely powdered ore was treated with a boiling mixture of two volumes of concentrated hydrochloric acid and one volume of water (galena dissolves at once in hot acid of this strength), nitric acid being added towards the end of the decomposition if pyrites was present. Volatile acids were expelled by evaporation with sulphuric acid. After the liquid had been diluted and boiled, the lead sulphate and insoluble matter were collected, and treated as already described. In the case of ore No. 3, which contained a fairly large amount of iron, double evaporation was performed. The presence of barium sulphate in No. 6 necessitated solution and reprecipitation of the lead sulphate.

For the gravimetric estimation, the decomposition of the ore was carried out in the same way until the lead sulphate and insoluble matter had been collected. The former was then extracted by washing the precipitate and paper with hot 20 per cent. solution of ammonium acetate. Lead sulphide was precipitated from the acetate solution by means of ammonium sulphide, collected, freed from iron by washing with a mixture of very dilute sulphuric acid and an aqueous solution of hydrogen sulphide, and dissolved in hydrochloric acid. Re-evaporation with sulphuric acid was then carried out. Finally, the lead sulphate was collected in a Gooch crucible, and dried at 150°.

The gravimetric estimation of lead in one ore—the mixture of galena and barytes—was found to be very difficult. Evaporation with sulphuric acid cannot be employed here. Extraction of all lead by means of hydrochloric acid is impracticable, because a small amount of lead sulphate is always precipitated with the barytes which separates out as the solution cools. Fairly satisfactory extraction of the lead was attained by attacking the ore with hydrochloric acid, evaporating almost to dryness, adding excess of sodium hydroxide, and filtering, this procedure being repeated with the residue. Lead sulphide was obtained, and dealt with as before.

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Of the specimens assayed, (1) was almost pure galena, (2) contained a little pyrites and some silica, (3) contained a little copper, and more iron pyrites, with a siliceous gangue, (4) consisted of galena, limonite, and silica, (5) was composed of about equal weights of galena and calcite, and (6) was the specimen of galena associated with barytes, already mentioned. Table VIII gives the results.

TABLE VIII.

No.	Method.	Lead per cent. found volumetrically.	Lead per cent. found gravimetrically.	Other constituents estimated. Per cent.
1.	A	84.2	84.3	
"	"	84.0		
2.	"	72.7	73.0	Fe=2.59; Cu=0.73
"	"	72.8		
3.	"	40.1	40.2	Fe=9.3; Cu=0.95
"	"	40.2		
4.	"	73.2	73.4	Fe= 3.4
5.	B	45.3	45.3	Ca=18.1
6.	"	72.3	72.1	Ba= 8.15

The method gives results which are very close to those obtained by the rather laborious operations of obtaining pure lead sulphate and weighing it, in about one-fourth of the time. Compared with the two principal volumetric methods in use—the molybdate and indirect dichromate methods—it has marked advantages. The molybdate process, in the simple form devised by Alexander, is a little more rapid, but gives erroneous results in the presence of calcium (Bannister and McNamara, *Analyst*, *loc. cit.*), and the end-point—which is never a definite one—is liable to be obscured altogether by the action of iron on the tannin. The present method requires much less time than the modification of Alexander's original process which has been devised by Low ("Technical Methods of Ore Analysis," 1911, p. 149) to avoid these difficulties; it is unaffected by the presence of large amounts of calcium, can readily be adapted to the assay of ores containing moderate amounts of barium, and is not liable to any unavoidable disturbance of the end-point.

The method which has been discussed in this paper is at once more rapid and more accurate than the indirect dichromate method, and is not subject to any constant error corresponding with that caused by the lead chromate being always precipitated in a form which is more or less basic.

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