mined in the usual way. Or the precipitate may be ignited and weighed, thus giving the combined weight of alumina added, of alumina in the mineral and of phosphoric acid in the mineral.

RESULTS ON KNOWN MIXTURES.

Mixtures were made by Prof. Campbell's private assistant which were strictly unknown to the operator, and were subjected to the above method of analysis with results as recorded in the following table:

	Weight of iron taken. Gram.	Al_2O_3 taken. Gram.	P_2O_5 taken. Gram.	$P_2O_5 - Al_2O_3$ taken. Gram.	P_2O_5 and Al_2O_3 found. Gram.	Gain or loss. Gram.
(1)	0.7023	0.00664	0.00077	0.000741	0.000735	0.00006
(2)	0.2020	0.1343	0.00022	0.13452	0.1343	0.00022
(3)	0.059934	0.0105	0.00576	0.01581	0.0162	0.00039
(4)	0.3339	0.0966	0.01072	0.10732	0.1066	0.00072
(5)	0.6604	0.030	0.00577	0.03577	0.03570	0.00007
(6)	0.551	0.05152	0.01073	0.06225	0.06220	0.00005
(7)	0.527	0.0219	0.01073	0.03263	0.0330	0.00037
(8)	0.564	0.0644	0.00822	0.07262	0.0719	0.00072

A solution was prepared by dissolving one gram of calcium carbonate, 0.200 gram magnesium carbonate, 0.571 gram of ferric oxide, and one gram of manganous chloride, in hydrochloric acid. To this solution, 0.09016 gram aluminum oxide, and 0.05234 gram of phosphorus pentoxide was added. The combined weight of alumina and phosphorus pentoxide taken was therefore 0.1425 gram. The weight found was 0.1428 gram.

UNIVERSITY OF MICHIGAN,
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THE DETERMINATION OF ANTIMONY IN ORES.

BY THOMAS BROWN, JR.

THE object of this paper is not to present new methods, but on the other hand the application of some very old ones which have been agreed upon by the buyers and sellers for determining antimony in ores, and which after trial have been proved to give more closely agreeing and satisfactory results than those formerly obtained by the many more widely used volumetric and gravimetric methods. In addition such observations and innovations in using these methods will here be mentioned as have been made by the writer in an experience of a year or so in analyzing the Mexican ores for the large exporters.

Only a limited number of commercial chemists both on this continent and in Europe are now engaged in doing this kind of work, because of the past wide variation in results frequently reported on the same sample, caused doubtless by the use of methods not so applicable to this class of ores, which is a matter of much importance considering the large shipments made from Mexico. The following list is of interest in showing the percentages of antimony reported on the same samples of Mexican ores by three prominent English commercial analysts before definite methods had been settled upon, and also the necessity for such a procedure. A, B, and C represent the results of these three chemists, B and C being of London, and D the percentage finally agreed upon in settling.

Sample No.	A.	B.	C.	D.
I	59.96	55.25	56.1	55.6
II	55.8	53.62	52.0	52.8
III	57.27	54.02	54.2	54.1
IV	58.13	54.5	54.8	54.6
V	60.78	59.23	63.1	60.0
VI	57.45	53.7	53.6	53.6
VII	....	53.5	54.4	53.9
VIII	59.8	53.2	54.9	53.5
IX	53.2	52.0	57.8	52.6
X	....	50.4	51.5	50.9
XI	....	52.4	53.7	53.0
XII	....	51.7	53.2	52.4
XIII	....	46.03	47.7	46.8

These ores are known to the trade as "clean ores," it being of rare occurrence to find impurities in the grades shipped other than silica, iron, and lime which obviously would not interfere with the schemes of analysis used. The metals of the fifth and sixth groups sometimes found accompanying antimony in ores, such as lead, mercury, copper, tin, and arsenic, when found in quantities larger than traces should be separated from the antimony when it is to be determined by the method used for sulphides, and also tin and arsenic when the antimony is to be determined by the oxide method. Shipments of ore from an unknown locality should consequently be put through a series of preliminary tests, and it is always advisable to test every sample for the most common impurities such as lead and arsenic; qualitatively for the purpose of modifying the sulphide method

and quantitatively if found in appreciable quantities, because of having to be taken into consideration in estimating the market value of the ore.

Lead is determined both qualitatively and quantitatively as the orange-yellow chromate ($PbCrO_4$). For the qualitative test the finely ground ore is boiled with concentrated nitric acid for several minutes, and, if a sulphide, until the sulphide of antimony is entirely converted into the insoluble white oxide, then cooled and diluted. Ammonia is added in excess, then acetic acid in excess, and the whole heated for several minutes in order to bring the lead salts thoroughly into solution. The insoluble matter is now filtered off, and the filtrate treated with an excess of potassium bichromate which precipitates the lead as chromate from this ammonium acetate and acetic acid solution. The lead can also advantageously be determined quantitatively in this form from the sulphide precipitate remaining on the filter after separating the antimony from the metals of the fifth group as will be explained later in the scheme of analysis.

For arsenic a combination of the Canby and Mohr methods is used. One gram of the finely powdered ore is mixed in a porcelain crucible with eight to ten parts of a mixture of equal parts of sodium carbonate and niter, gradually brought to fusion over a burner or in a muffle and kept so for five minutes or more. The fused mass is allowed to cool, disintegrated in hot water and the insoluble matter filtered off. The filtrate is now acidified with nitric acid and the carbonic and nitrous acid gases boiled off. An excess of an emulsion of zinc oxide, so apparent in the bottom of the beaker, is added, and should an unusually heavy precipitate of gelatinous silica and alumina be produced, a second filtration is necessary, also an extra addition of zinc oxide to the filtrate before the precipitation of the arsenic. This is precipitated as the reddish brown silver arsenate (Ag_3AsO_4) by the addition of silver nitrate in slight excess accompanied by vigorous stirring.

The precipitate mixed with zinc oxide is filtered, washed with cold water until the washings show no silver reaction, and dissolved off the filter with hot dilute nitric acid, catching the solution and washings in a beaker free from chlorine. When cold this is titrated for silver with an empirical solution of potassium

or ammonium thiocyanate using one cc. of a saturated solution of ferric sulphate as indicator, and titrating to the same pale amber-yellow color as was obtained in standardizing the solution against pure silver. For the standard silver solution one gram of the pure metal is dissolved in nitric acid, boiled to expel red fumes and diluted to 100 cc. For the standard thiocyanate solution nine and three-tenths grams of potassium thiocyanate or seven and six-tenths grams of ammonium thiocyanate are dissolved and diluted to one liter ; then 1 cc. $=$ 0.010 gram silver, and 108 silver $=$ 25 arsenic. This same treatment somewhat modified is used in testing the ore qualitatively for arsenic. After fusion, the addition of acid, boiling and the addition of zinc oxide in excess, the whole is filtered and the neutral filtrate tested for arsenic as before.

The antimony ores of Mexico most common to the trade are those of stibnite (Sb_2S_3); cervantite (Sb_2O_4) produced by the oxidation of the former; oxysulphides, mixtures of these two with a preponderance of the former, and senarmontite (Sb_2O_3) which is, however, of much rarer occurrence. The composition of the oxide may be inferred from its behavior when boiled with concentrated hydrochloric acid with the subsequent addition near the end of the treatment of a few drops of nitric acid. Cervantite treated thus is but sparingly soluble, while senarmontite is almost if not completely so. Stibnite is also completely soluble ; if, however, the ore be an oxysulphide as is frequently the case, insoluble oxide of antimony is found in the siliceous residue which is afterwards determined by fusion.

The following analysis of an ore from the state of Oaxaca illustrates this statement in regard to the solubility of these oxide ores : Moisture, 0.3 ; silica, 8.5 ; iron oxide and alumina, 1.6; iron pyrites (FeS_2), 0.9 ; lime and magnesia, traces ; cervantite (Sb_2O_4), 3.8 ; senarmontite (Sb_2O_3), 84.7 ; total, 99.8. The results of a complete analysis being calculated to their probable composition, left a difference of 88.7 per cent., to be filled by the 70.8 per cent. soluble and the three per cent. insoluble antimony found, and which were calculated to the composition of senarmontite and cervantite as they were shown to be by their solubility.

Upon the behavior of these ores when treated with concentra-

ted hydrochloric acid plus a few drops of acid and boiling, is based their division into the following three classes for applying the schenies of analysis : 1. The soluble ores—stibnite (and senarmontite) ; 2. The practically insoluble ores—cervantite ; 3. The partially soluble ores—the oxysulphides, stibnite mixed with cervantite.

1. *The Soluble Ores.*—For the *"soluble ores"* one gram, which has been finely pulverized in an agate mortar, is treated in a No. 3 beaker with twenty-five cc. concentrated hydrochloric acid, covered and boiled on a plate or over a flame until apparently decomposed and the solution is not more than fifteen cc. in bulk. About two grams of tartaric acid are added, and as soon as that is dissolved about four to six drops of concentrated nitric acid, and the whole is boiled for a minute or so more. This last addition causes a violent reaction and a more complete decomposition. The beaker is now removed from the source of heat, the cover and sides washed down, the insoluble residue filtered out and the filtrate and washings diluted in bulk to about 250 cc. A steady stream of hydrogen sulphide gas is now run through the solution for about an hour until it is thoroughly saturated and the antimony thus precipitated as the amorphous orange-colored sulphide (Sb_2S_3).

To insure a complete precipitation this is gently warmed in order to convert any basic chloride into sulphide and then allowed to stand an hour or so in the cold before filtering. The filtrate will then be perfectly clear and not deposit additional antimony upon standing or upon further treatment with hydrogen sulphide gas. Should lead or other impurities of the fifth group have been found by the preliminary qualitative tests, after filtering and washing the precipitate with cold water it is washed back into the beaker in which it was precipitated and treated with ammonium sulphide in such excess that with the aid of heat the antimony precipitate completely dissolves. The solution is then run back through the same filter, caught in a clean beaker and the filter thoroughly washed with hot water. The solution and washings are acidified in slight excess with hydrochloric acid, reprecipitating the antimony sulphide, diluted to about the same bulk as before (250 cc.), allowed to stand a few minutes to settle and then filtered. In the black sulphide

residue remaining on the filter representing the impurities of the fifth group, the lead may now be determined by placing the filter containing this precipitate into a beaker, treating with nitric acid and boiling, adding ammonia in excess, then acetic acid in excess, filtering, reprecipitating the lead as chromate and weighing it thus on a Gooch crucible or balanced filter-papers.

The antimony sulphide precipitate, whether precipitated but once or reprecipitated for purification, is now washed well upon a large, plaited, balanced filter with cold water and dried in an air-bath at 110° C. for two hours or more to constant weight. After removal and as soon as cold the weight of the dried precipitate is taken which consists of antimonous sulphide (Sb_2S_3) mixed with a small amount of free sulphur.

The following procedure has been found both rapid and accurate for weighing this precipitate. A German corrugated filter, 15 cm. in diameter, is used. Two are selected which lay beside one another in the same pack and which from long impact contain practically the same amount of moisture. They are balanced by cutting down the heavier one. Upon the unaltered one the precipitate is filtered, the other accompanying it in the drying oven and as a counterpoise in weighing. When the weight of the precipitate has thus been determined it is carefully scraped from the paper and powdered and mixed well by grinding in a small glass mortar. A certain amount of this (five-tenths gram) is weighed off into a platinum boat, this introduced into a glass combustion tube and the free sulphur driven off in a stream of carbon dioxide. From the weight of the resulting black anhydrous antimonous sulphide so obtained on a weighed amount of the dried precipitate, its total weight thus treated can easily be calculated, and it is then simply a matter of calculation to determine the total amount of antimony present. $Sb_2S_3 \times 0.7177 = Sb$.

The combustion requires in all from twelve to fifteen minutes, and if carefully conducted with the following precaution, very little loss if any at all occurs. Arsenic if present would be volatilized. (a) A steady stream of gas should be passing through the tube when the flame is applied underneath the boat, and should continue so with as little variation as possible until the end of the operation. Should this not be the case, a flame

would at first play over the surface of the contents of the boat causing oxidation apparent to the eye when removed from the tube by a whitening of the surface and consequently a loss in weight. (*b*) The heating of the boat in the tube should be accomplished gradually. At first a gentle heat is applied until all the sulphur has apparently been driven off, and increased towards the end of the operation. (*c*) The tube should be cleaned of sublimed sulphur by heating before each and every determination. After weighing the boat and contents it is well to treat again for additional loss in weight, which is rarely found if the operation has been conducted as described.

2. *The Practically Insoluble Ores.*—The important point here is the decomposition of the ore which is accomplished by fusion. One gram of the finely powdered ore is mixed with eight to ten parts of a flux composed of equal parts of flowers of sulphur and sodium carbonate, introduced into a porcelain crucible (capacity forty cc.), and in addition the mixture is covered with a thin layer of the flux. The covered crucible is introduced into the opening of a muffle that is of a bright red heat and is cautiously heated to fusion for about ten minutes. The heat applied at first should be of such an intensity that sulphur flames are barely seen escaping around the edge of the lid; after they cease it is somewhat increased by pushing the crucible a few inches farther back in the muffle. At no time should the crucible become heated to more than perceptible incandescence on the side facing the source of heat, and during the operation it should be occasionally turned with a pair of tongs to insure an even heating and consequently a complete decomposition. The color of the melt when cold should be green, not yellow, and likewise the solution of the same due to the sulphide of iron present. A suggestion of a yellow color particularly in the solution indicates an incomplete decomposition of the ore, and but a partial change of the antimony into the soluble sodium sulphantimonate which consequently necessitates a repetition of the fusion.

A successful fusion owing to the ready volatility of antimony at a comparatively low degree of heat is rather a delicate thing and difficult to accomplish, requiring constant care and judgment only gained by experience. With the statement that it is possible to thoroughly decompose such an ore by fusing over a

candle flame, the writer is compelled to differ, having frequently found that a fusion made at a seemingly alarming degree of heat gave when dissolved a yellow solution in which the antimony when determined was found to be lower than that of a duplicate sample which had been treated to a higher degree of heat. It is, therefore, better to treat in excess than not to fuse enough ; for should there be a slight loss by volatilization, this would in a measure be counterbalanced by the small amount of impurities, such as silica, obtained from the action of the flux on the crucible and on the silica of the ore, and consequently thrown down by the acid and weighed with the antimony sulphide precipitate. The degree of heat used, however, should scarcely effect the glaze of the crucible. When the fusion has thus been satisfactorily accomplished and when cool, it is dissolved in hot water, which takes but a few minutes, thes uspended precipitate of iron sulphide and sulphides of the metals of the fourth group, if present, filtered off, and the antimony precipitated by adding a slight excess of hydrochloric acid to the filtrate. After stirring and allowing to stand a few minutes to settle the precipitated antimonic sulphide (Sb_2S_5), mixed with more or less free sulphur, is filtered off upon a balanced filter and so determined as before, being ultimately weighed when removed from the combustion tube as antimonous sulphide (Sb_2S_3).

3. *The Partially Soluble Ores.*—These ores require a double treatment, that is they are first treated as for soluble ores and the antimony determined in the acid solution, and the residue, remaining on the filter which contains the undissolved oxide, is subjected to a fusion as for oxide ores. This filter-paper is placed in the bottom of a porcelain crucible and covered well with flux so that some comes in direct contact with its contents. It is then fused as directed. In dissolving, pieces of charred paper may possibly be found. which are, however, filtered out together with the insoluble matter. The amount of antimony so present is determined as before.

Most Mexican so-called sulphide ores exported are really oxy-sulphides being mixtures of sulphide with a small amount of oxide which has not been separated in the sorting ; these ores consequently require this double treatment. The following is a list of results obtained in using these methods upon the pre-

viously mentioned varieties of Mexican ores, and gives in the case of oxysulphides the soluble and insoluble antimony found. In the last column will also be found the results by the fire assay, which is extensively used on oxide ores for prospecting work, and also for large shipments when the "wet assay" is to be made later at their destination. It is figured by the dealers that the wet assay of a sixty per cent. ore will go six per cent. higher than the dry or fire assay. That there are exceptions to this will be seen in Nos. 5, 8, and 12 of the table. No. 5 is the senarmontite ore, the complete analysis of which has already been given, while Nos. 8 and 12 are quite insoluble under the acid treatment leading to the supposition that they are cervantite ores of the composition Sb_2O_4. It has also been observed that certain grades of oxide ores give higher results by fire assay than other grades, which is considered due to their ultimate composition of which very little is so far known. The widely different and extremely low results obtained by fire assay upon sulphide ores makes them no criterion upon which to judge of the actual antimony present, and so for this class of ores it is falling into disuse.

No.	Class of ore.	Soluble Sb.	Insoluble Sb.	Total Sb.	Fire assay.
1.	Sulphide	67.4	..	67.4	....
2.	"	28.5	..	28.5	....
3.	Oxysulphide	61.6	5.1	66.7	48.0
4.	"	63.3	6.7	70.0	45.0
5.	Oxide	70.7	3.1	73.8	72.8
6.	"	...	..	71.7	65.0
7.	"	...	..	66.1	59.0
8.	"	...	..	63.9	61.8
9.	"	...	..	55.8	49.0
10.	"	...	..	49.0	43.0
11.	"	...	..	48.3	43.0
12.	"	...	..	46.4	44.4

The fire assay referred to consists of the reduction of the contents of the ore to the metallic state by fusion with potassium cyanide and while it is known that it is possible to obtain higher results by the use of other mixed fluxes together with a treatment for a longer time at a lower heat, this cyanide reduction remains the accepted method in trade. It is performed as follows : Five grams of the powdered ore is mixed with twelve

parts of potassium cyanide, placed in a ten gram clay crucible and covered with salt. The fusion is made in a muffle at a bright red heat, allowing it to remain there thirteen minutes. When removed it is thoroughly shaken to collect the globules into one metallic button and allowed to cool. The crucible is broken and the resulting button carefully broken from the slag and weighed.

In conclusion the writer desires to express his obligation both to Mr. M. Elsasser and to Mr. Ferdinand McCann for their kind assistance in furnishing him with suggestions, data, etc., without which this paper would not have been written.

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ELECTROLYTIC DETERMINATION OF ZINC IN THE PRESENCE OF MANGANESE.

BY EMIL J. RIEDERER.

IN determining zinc quantitatively by means of the electric current, it is essential to have the zinc in the form of sulphate and there should be neither nitrates nor chlorides present.

It was found best to use a platinum dish, on which silver had been deposited, for a cathode. In the first experiments, I tried copper deposits on platinum, but discarded this owing to the fact that copper is too easily oxidized, and consequently causes variation in weight. During the deposition of zinc it is found best to stir the solution (using a mechanical stirrer) continually, so as to obtain an even and uniform deposit ; and to keep the temperature under 26° Celsius.

The current used for the deposition of zinc was four volts, giving a current of three and five-tenths volts and 0.20 to 0.26 amperes for 100 sq. cm. of cathode area. The current may vary from 0.20 to 0.26 amperes and the temperature from 15° to 26° Celsius.

Different proportions of zinc and manganese were tried so as to determine the action of the manganese, but in no case could any traces of manganese be found in the zinc which was deposited on the cathode.

The following reagents were used for the electrolysis:

a. A solution of lactic acid ($CH_3.CHOH.COOH$,   each