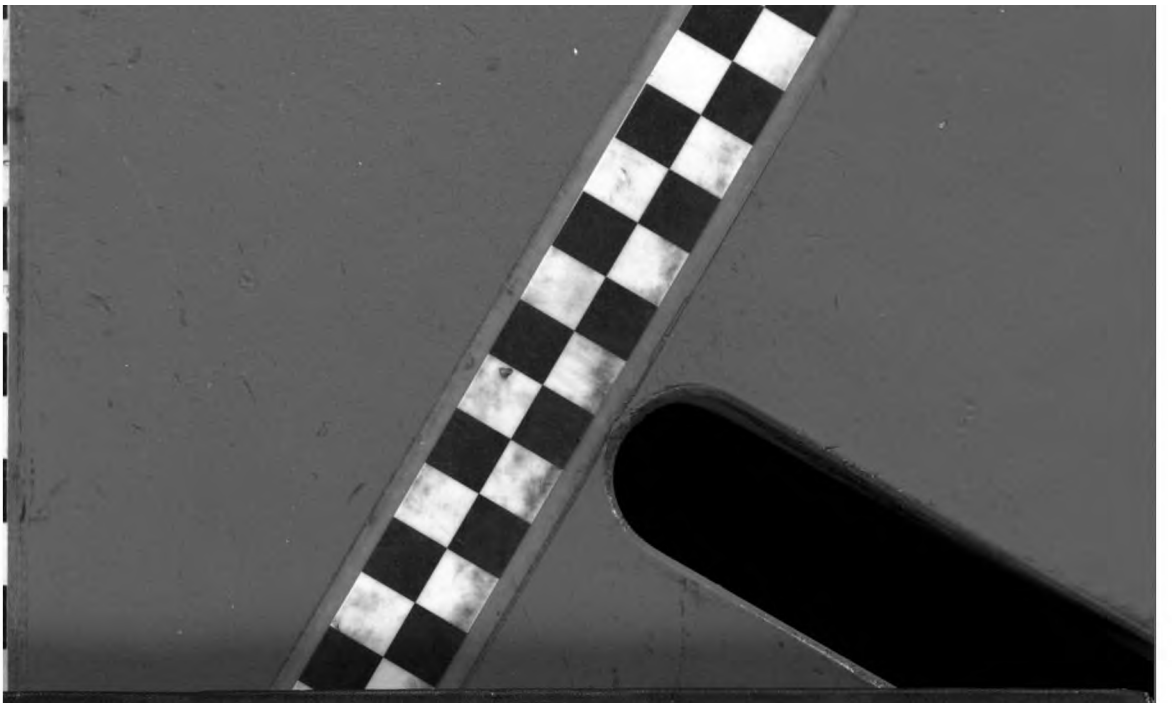

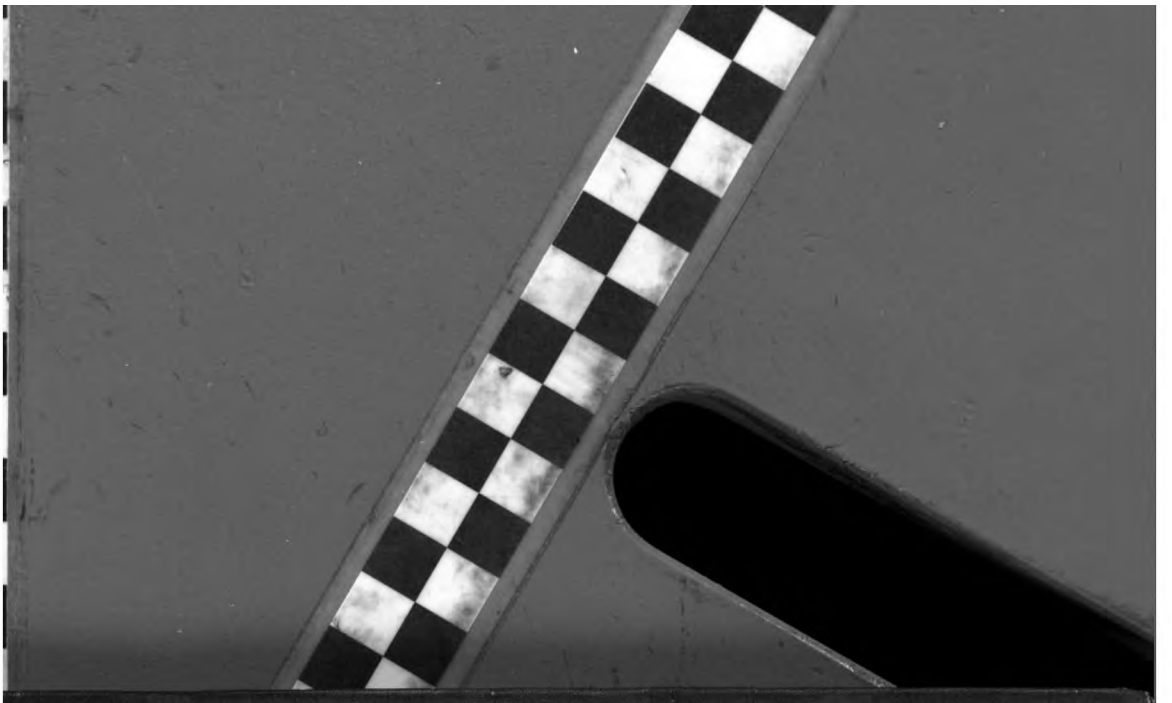

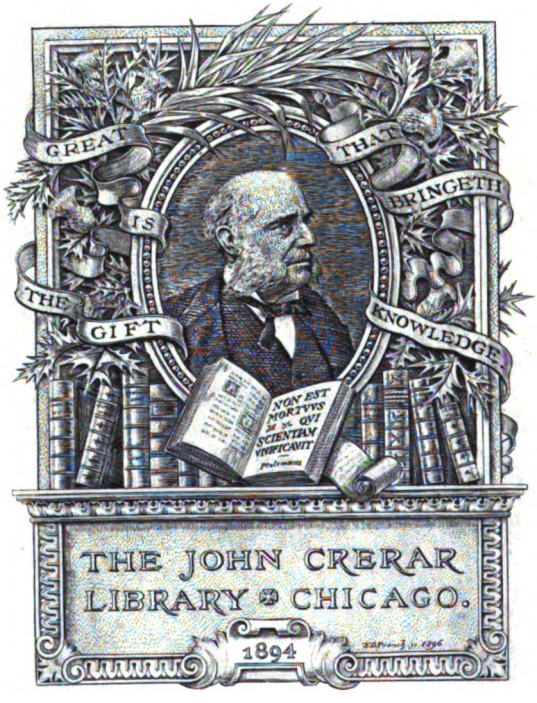

Rapid Methods of Technical Analysis

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Rapid Methods of Technical Analysis

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In June, 1892, the writer published in the "Scientific Quarterly" of the Colorado School of Mines, some "Quick Assay Methods," which were in use in many of the smelting establishments of the western part of the United States. Since then many new methods have been devised or developed, and many old methods improved; chemists, assayers, scientific societies and periodicals having worked in harmony and with enthusiasm for the purpose of developing simple, rapid and exact methods, and at the same time, avoiding the use of complicated and costly apparatus and noxious reagents.

Under the above title it is attempted to compile the most modern methods at present in use for the determination of the principal constituents of ores and metallurgical products. The writer has endeavored to give credit to the sources of information, and should there be found omissions in this respect, he would be glad to have his attention called to them. Should the publication of these methods contribute in even a slight degree to the development of the Mining and Metallurgical industry, the writer will feel gratified.

METHODS

INSOLUBLE RESIDUE.

1. Half a gram of the powdered sample is placed in a small beaker or casserole of about 250 cc. capacity, and treated as follows: If the substance is a sulphide, 5 cc. of water, 10 cc. of HNO_3 and about 1 gram of chlorate of potash are added and the mixture heated without boiling until decomposition of pyrites has been effected, when 5 cc. of HCl are added, and the solution evaporated to dryness.

2. If the substance is an oxide, or mixture of various kinds, or of oxide with sulphide, 10 cc. of HCl are added and gently heated until oxides of iron are dissolved, then 3 cc. of HNO_3 and, if necessary, a little chlorate of potash is added to decompose any globules of sulphur formed, and the mixture evaporated to complete dryness.

3. When dry it is cooled, 10 cc. of HCl added and the contents gently boiled a few minutes; about 50 cc. water are added, again boiled and filtered, decanting onto the filter as much as possible of the clear solution and allowing it to run through before transferring the residue to the filter, which is then washed several times with hot water, allowing each wash to run through the filter before adding the next wash water.

4. The beaker containing the soluble substances, is covered and set aside for the determination of Alumina. (See paragraph 16.)

5. The insoluble residue on the filter may contain the following substances in addition to all of the silica: chloride and sulphate of lead which are soluble in ammonium acetate, chloride of silver and tungstic acid which are soluble in ammonia, sulphate of barium and oxide of tin, which are insoluble in all acids, including hydrofluoric, and that part of the alumina in the form of sili-

cate, this being soluble in hydrofluoric acid. Another beaker is placed under the filter, which is then washed with hot water and ammonium acetate and afterward with hot water containing ammonia in order to dissolve out lead, silver and tungsten, which of course are rejected.

6. The filter containing the insoluble residue is placed in an annealing cup or platinum crucible, dried, burnt to eliminate the paper and weighed, the number of miligrams of weight multiplied by 0.2 gives the percentage of insoluble residue.

SILICA, SiO_2.

7. The insoluble residue is placed in a weighed platinum dish or crucible and evaporated to dryness, with about 3 cc. HCl and 5 cc. of hydrofluoric acid. The evaporation is repeated with the same acids until a constant weight is obtained, thus proving that all of the silica has been volatilized; the loss of weight therefore represents the percentage of silica.

The residue left in the crucible contains that portion of the alumina insoluble in acids, but which is now soluble, it is then dissolved in HCl and added to the solution mentioned in the 4th paragraph. The acids employed in the volatilization of the silica should leave no residue when evaporated to dryness on platinum.

8. Many chemists prefer the fusion of the insoluble residue with carbonate of soda. To do this the insoluble residue is mixed in a small platinum crucible with about 3 grams of carbonate of soda, the crucible is covered and contents fused at a high temperature in a muffle or over a blast lamp, the bottom of the crucible is quickly cooled in water, about 5 cc. of hot water is added and gently heated to loosen the fused mass from the crucible, which is then transferred to a casserole, using a minimum quantity of water for the purpose, it is then heated until completely disintegrated and also to evaporate the greater part of the water.

9. The mass is then neutralized with HCl and about 3 cc. excess added and evaporated to dryness, the evaporation being repeated with another addition of about 3 cc. of HCl after cooling the casserole; finally 5 cc. HCl and about 50 cc. of water are added, the solution boiled, filtered, washed and the filter dried, burnt and weighed.

10. In the fusion method, the silica is liable to contain some of the barium sulphate, supposing that the original substance contained barium sulphate, and this must be determined and subtracted from the result obtained according to paragraph 9.

IRON, Fe.

11. A convenient method for determining iron is a modification of that attributed to Peeny. For this, the following solutions are necessary: 4.385 grams of bicromate of potash are dissolved in a little hot water and diluted with cold water to 1 litre; 1 cc. of this solution is equivalent to about 5 miligrams of iron in titration. Ferri-cyanide of potash, about 0.1 gram dissolved in 50 cc. water. (This salt should be free from ferro-cyanide.)

12. To standardize the solution of bicromate 200 miligrams of pure iron are dissolved in about 10 cc. of HCl and a little water, about 5 grams of pure granulated lead and 50 cc. of water added and boiled gently a few minutes, the solution allowed to cool and is then decanted from the lead, which is washed three times with cold water and the solution is then titrated with the bicromate

solution, using the solution of ferri-cyanide as an indicator on a drop plate. The analysis is ended when a drop of the iron solution barely ceases to give a blue tinge when brought into contact with a drop of the indicator on the drop plate. The number of miligrams of iron taken, divided by the number of cc. of bicromate employed, gives the oxidizing power of 1 cc. of the solution; this point is mentioned because practically all chemists have, at least once in their experience, incurred the error of reversing this calculation.

13. In the analysis, half a gram of the sample is decomposed as described in paragraphs 1 or 2, but in case that it should not be necessary to employ other acids than hydrochloric, it will not be necessary to evaporate the solution to dryness; on the other hand, if nitric acid is used, it is absolutely necessary to expel all of the acid and break up all nitrates by evaporation to dryness, by a second evaporation with about 5 cc. of HCl. The residue is then dissolved in about 10 cc. of HCl and 50 cc. of water, about 20 grams of granulated lead added and gently boiled until the solution is completely colorless. The solution is then freed from the lead and titrated as described in the preceding paragraph.

14. In order to obtain the greatest accuracy, it is necessary to make a blank analysis, using the same quantities of all the reagents employed in the actual analysis, but with none of the sample. This is the simplest means of determining if the reagents contain iron or substances which might score as iron in the analysis; any result thus obtained is kept on record and deducted from each result obtained in the analysis. This procedure is likewise advisable in all the volumetric methods to be described further on.

15. In the above method, copper, arsenic and antimony are precipitated on the lead and thus eliminated as disturbing or interfering factors; cromium and titanium interfere, but are seldom met with, especially in ores of gold, silver, copper and lead.

ALUMINA, Al_2O_3.

16. The residue mentioned in the last part of paragraph 7 is moistened with about 5 cc. of HCl and added to the solution mentioned in paragraph 4. The whole is neutralized with ammonia, about 5 cc. in excess added, boiled, allowed to settle, decanted on a filter and washed several times with hot water containing ammonia. (It may be well to mention here that it is useless to wash hydrates with water only.) The solution in the beaker is set aside for the determination of lime and magnesia.

17. As much of the precipitate as possible is transferred to a clean beaker by means of a stream of water from the wash bottle and without removing the paper from the funnel; this beaker is placed under the filter and the filter treated with a solution of about 5 cc. sulphuric acid diluted in about 25 cc. of water to dissolve any precipitate remaining in the pores of the filter paper; the contents of the beaker are then boiled and examined and if any residue remains undissolved, as for instance, sulphate of lead, it is necessary to filter the solution to eliminate said residue.

18. To the clear solution is added 5 cc. of HCl, it is then boiled and again treated with ammonia, boiled, filtered and washed as before with hot water containing ammonia.

19. The contents of the beaker are added to the beaker mentioned in the last line of paragraph 16.

20. The precipitate and filter paper are placed in a weighed platinum dish and the paper burnt at as low a temperature as possible, the dish and precipitate are weighed and the increase of weight represents Al_2O_3, plus Fe_2O_3.

21. The precipitate is dissolved in HCl, transferred to a beaker and the iron determined as per paragraph 12. The Fe obtained multiplied by 1.43 gives its equivalent in Fe_2O_3, and this subtracted from the combined weight mentioned in the last paragraph, gives the Al_2O_3 by difference.

22. Interfering elements are: phosphorus, cromium, titanium, antimony and arsenic. The first four are seldom met with, but arsenic is more common, being found in pyrites, mispickle, etc. It is necessary to use special methods to eliminate them, but for the moment it will suffice to describe one for separating out the arsenic. The sample is decomposed in acids, 5 cc. of sulphuric acid added and evaporated to dense white fumes, after cooling, 10 cc. water, 10 cc. HCl and about ½ gram of bi-sulphite of ammonia or soda are added and the mixture evaporated again to white fumes. In this operation all of the arsenic and most of the antimony is volatilized.

23. Five cc. of HCl, 5 cc. of HNO_3 and 50 cc. of water are now added, the solution boiled and filtered as described in paragraph 3.

MAGNESIA, MgO.

24. A current of hydrogen sulphide is passed into the beaker of solution mentioned in paragraph 19, to precipitate lead, copper, etc., it is then heated, the precipitate allowed to settle, filtered and washed; the filtrate boiled to expell the excess of gas after having acidified it with HCl; 3 cc. of HNO_3 are added to oxidize the sulphur and after boiling, 3 grams of oxalate of ammonia are added, the solution made ammoniacal and boiled about 15 minutes at a gentle heat, the oxalate of lime filtered off and washed with hot water containing ammonia and ammonium chloride. In analysing dolomite, magnesite or other substances containing much magnesia, it is necessary to redissolve the calcium oxalate in HCl and reprecipitate the lime as before, combining the two filtrates for the determination of the magnesia.

25. To the combined filtrates about 3 grams of phosphate of ammonia or double phosphate of soda and ammonia are added and about 100 cc. of strong ammonia; the solution is mixed by pouring it backward and forward between two large beakers (stirring with a glass rod causes the precipitate to adhere to the sides of the beaker), the solution is diluted with cold water to about 600 cc. and allowed to stand in a cool place over night, or a couple of hours in a refrigerator; the precipitate is then filtered off, washed many times with cold water containing ammonia, burnt and weighed as $Mg_2P_2O_7$, this weight multiplied by 0.3624 gives the equivalent in MgO.

LIME, CaO.

26. Lime is determined by titration with potassium permanganate. The standard solution is prepared by dissolving 5.88 grams of the salt in about 200 cc. of hot water and diluting with cold water to 1 litre; 1 cc. of the solution has a value of about 5 miligrams of CaO. (1 cc. also has a value of about 10 miligrams of Fe, and 2.95 miligrams of Mn.)

27. To standardize the solution, pure iron wire is cleaned with emery paper and exactly 200 miligrams dissolved in about 50 cc. water and 10 cc. H_2SO_4,

using a small flask with a rubber cork containing a small aperture which will allow the steam to escape and at the same time expel the air from the flask while the iron is dissolving. About 150 cc. of hot water are then added and the solution quickly titrated with the solution of permanganate until a final drop produces a slight pink tinge. The factor for CaO is one-half of the factor for Fe.

28. The solution may also be titrated with freshly-dried oxalic acid; 225 miligrams have the same reducing power as 200 miligrams of Fe, 100 miligrams of CaO as oxalate, or 59 miligrams of Mn. To standardize, dissolve 225 miligrams in hot water, add 150 cc. cold water and 10 cc of H_2SO_4, heat and titrate as before.

29. For the direct analysis for lime dissolve half a gram of the sample in acids and after evaporating nearly to dryness, add 10 cc. HCl and 100 cc. hot water; ammonia is then added, drop by drop, with stirring until the color begins to change to red, a few drops are added until a small precipitate, only, of iron is formed. The object is to neutralize all free acid without precipitating much iron. Three grams of ammonium oxalate are now added and the solution boiled vigorously until the iron is dissolved and the precipitate made granular. The beaker is now filled with hot water, the precipitate allowed to settle and then filtered and washed with hot water and ammonia until the washings fail to discolor a drop of permanganate when acidified with H_2SO_4, thus indicating that the excess of ammonium oxalate has been washed out of the precipitate of calcium oxalate.

30. To the beaker in which the precipitation was effected is now added about 100 cc. of water and 10 cc. of sulphuric acid which is heated and the precipitate of calcium oxalate transferred to it by a stream of water, the precipitate is allowed to dissolve and then titrated while hot with the solution of permanganate until the end point is reached; the filter paper is then added to the beaker and the titration rapidly completed. It takes several minutes for the paper to commence decomposing the permanganate, so that it is easy to complete the titration before it has effect.

31. The lime may also be determined by adding oxalate of ammonia to the filtrates mentioned in paragraphs 16, 18 and 19, and then continuing as described in paragraph 29.

32. The most common interfering element is lead. To eliminate this, the precipitate of calcium oxalate is dissolved in about 5 cc. of HCl, about 100 cc. of water added and the lead precipitated with H_2S; the solution is gently warmed and filtered, ammonia added and about ½ gram of oxalate of ammonia and the determination finished as in paragraph 29. The method as described in paragraph 29 recovers all lime which may be in the form of flouride or phosphate, whereas, in the common method of precipitating with ammonia and filtering off the iron, the fluoride or phosphate of calcium is precipitated along with the iron and lost as far as the correct determination of total lime is concerned.

MANGANESE, Mn.

33. (Volhard's Method Modified.) In a beaker or flask of about 400 cc. capacity, half a gram of the sample is dissolved in 10 cc. water and 10 cc. HCl at a gentle heat, half a gram of chlorate of potash added and the solution boiled almost to dryness to expel free chlorine and thoroughly oxidize the iron;

5 cc. of HCl are then added with a little water and boiled a few minutes, then about 200 cc. of hot water are added and about 30 grams of pure zinc oxide previously moistened in about 50 cc. of hot water. The solution is maintained at the boiling point during the titration with potassium permanganate and is agitated vigorously after each addition of permanganate until upon allowing the brown precipitate to settle a permanent but faint pink color in the supernatent liquor indicates the end point. The iron factor of the standard solution multiplied by 0.295 gives the factor for Mn. There are no interfering elements, but it is necessary to oxidize the iron and expel all free chlorine.

BARIUM SULPHATE, $BaSO_4$.

34. The insoluble residue is determined on half a gram of the sample as per paragraph 1, which is then fused with carbonate of soda as per paragraph 8. The melt is dissolved in hot water, filtered and washed to eliminate all sulphate of soda. The precipitate of barium carbonate is dissolved in dilute HCl and freed from any residue by filtration, 1 cc. of sulphuric acid is added to precipitate barium sulphate which is made granular by boiling, filtered, washed, burnt and weighed as $BaSO_4$.

35. To determine barium oxide (BaO) in slags, add 50 cc. of hot water to half a gram of the chilled sample of slag, and while boiling and stirring add 10 cc. of HCl; the solution is boiled a few minutes and quickly filtered while hot and dilute; after washing with hot water 1 cc. of sulphuric acid is added, the solution boiled about five minutes and the sulphate of barium filtered off and weighed as before. The solution should be kept hot and dilute to prevent precipitation of gelatinous silica. The weight of $BaSO_4$ multiplied by 0.657 gives BaO. The complete analysis of slags will be given in a special chapter.

COPPER, Cu.

37. A solution of potassium cyanide is made by dissolving 21.15 grams of pure salt in hot water and diluting to 1 litre; 1 cc. of the solution has a value of about 5 miligrams of copper or 1 per cent. on a half gram charge.

38. To standardize it, 100 miligrams of pure copper are dissolved in 5 cc. (measured) of nitric acid and about 15 cc. water, gently boiled to expel red fumes, 50 cc. cold water and 10 cc (measured) ammonia are added, the solution cooled to room temperature and then titrated with cyanide until the blue color begins to dissappear; the solution is then diluted to about 150 cc. and after waiting five minutes the titration is completed until only a very faint lilac tinge remains.

39. For analysis, half a gram of sample is taken and if it contains no sulphides is dissolved in 5 cc. water, 2 cc. nitric acid and 7 cc. of sulphuric acid and evaporated with a strong heat several minutes after heavy white fumes have appeared; it is then cooled and 5 cc. of water added, and should red fumes appear, it is necessary to again evaporate it to heavy white fumes.

40. If the sample contains sulphides it is best to dissolve in 7 cc. water, 7 cc. of nitric acid and 1 gram of chlorate of potash, evaporating it slowly almost to dryness; 5 cc. water and 7 cc. H_2SO_4 are then added and it is evaporated with much heat until the appearance of the dense white fumes, already mentioned.

41. In each case it is now cooled; about 100 cc. of water and a few pieces of aluminium, $1'' \times 2'' \times \frac{1}{8}''$ in dimensions, are added and the whole kept at a

gentle heat for twenty minutes or until the precipitated copper becomes detached from the aluminium. The beaker is then filled with hot water, the precipitate allowed to settle and the clear solution decanted, the pieces of aluminium are lifted out and washed with a stream of water so that the copper falls into the beaker which is again filled with hot water and again decanted. The beaker now contains all of the copper and insoluble residue, there having been eliminated by decantation the iron, nickel, cobalt, manganese, lime and above all, the zinc. The precipitate of copper is dissolved and titrated exactly as described in paragraph 38, employing the same quantities of reagents, the same time, and the same volume of solution at the end.

42. In this method, only the silver scores as copper, and this is generally neglected unless the silver assay exceeds about 80 ounces to the ton, in which case, 1 drop of hydrochloric acid is added with the 100 cc. of water mentioned in paragraph 41; it is then gently boiled, settled and an additional drop added to prove that all silver has been precipitated as chloride, it is then filtered, washed with hot water, the pieces of aluminium added to the solution and the precipitation and titration finished as before mentioned.

43. Direct Cyanide Method. The method in use in many places, of discolorizing with cyanide without previous precipitation, is absolutely incorrect if the sample contains zinc, nickel, cobalt, manganese, silver or organic matter; but once proven that these elements are absent, and taking the precaution to have the same conditions in the standardizing as in the assay, the results are correct. The *modus operandi* is as follows: Half a gram of the sample is decomposed in 5 cc. of water and 5 cc. nitric acid, if it is an oxide, or in 5 cc. water, 7 cc. nitric and 1 gram of chlorate of potash, if a sulphide; in both cases it is evaporated almost to dryness, cooled, exactly 5 cc. nitric acid and about 15 cc. water added, boiled to expel red fumes, about 50 cc. of water and exactly 10 cc. of ammonia added and it is then titrated rapidly with cyanide until nearly all of the color has faded; it is then filtered, the washing being dispensed with, as the amount of unfaded copper remaining in the pores of the precipitate is negligible. After filtering, the solution is diluted with cold water to a volume of 150 cc. and the titration concluded; the total time consumed in titrating and filtering should be about five minutes or the same time as that consumed in standardizing the cyanide solution.

44. Iodide Method. A solution of hyposulphite of soda is prepared by dissolving 20 grams of the salt in 1 litre of water. One cc. is equivalent to about 5 miligrams of copper or 1 per cent. when half a gram of initial charge is taken for assay. A starch solution is also prepared, as follows: About 20 cc. of cold water are added to 2 grams of starch and as soon as the starch is disintegrated, about 150 cc. of hot water is added and the solution boiled; it is then allowed to settle for about an hour and the clear solution decanted for use as an indicator.

45. In the assay, the copper is separated by precipitation on aluminium as described in paragraphs 39, 40 and 41. The precipitated copper as well as the 100 miligrams of pure copper for standardizing the hyposulphite solution are then treated separately as follows: Five cc. nitric and 5 cc. of water are added, the red fumes expelled by boiling nearly to dryness, 20 cc. of water are added and the solution neutralized with ammonia, it is then boiled to expel all odor of ammonia, neutralized with acetic acid and an excess of this latter added

drop by drop until all precipitate of copper is dissolved. (Mr. E. C. Kendall, in the December, 1911, number of the Journal of the American Chemical Society, recommends destroying nitrous acid by the addition of sodium hypochlorite and phenol.) About 100 cc. of cold water, 3 grams of potassium iodide and 2 cc. of the starch indicator are now added and the solution titrated with the hyposulphite of soda solution until the disappearance of the blue color by a final drop of the hyposulphite solution. There are no disturbing elements, but precautions must be taken to expel nitrous acid and free chlorine.

TIN, Sn.

46. Pearce-Low Method. A solution of iodine is prepared by dissolving 10.66 grams of metallic iodine, and 20 grams of potassium iodide in about 50 cc. of hot water and then diluting to 1 litre with cold water. One cc. of this solution is equivalent to about 5 miligrams of tin,or 1 per cent. on half a gram of charge.

47. To standardize, 100 miligrams of pure tinfoil are dissolved in hydrochloric acid, about 200 cc. of hot water and 4 to 6 cut iron nails, or, better still, a small chain of pure iron, are added and the whole gently heated without boiling for about twenty minutes, 10 cc. more of hydrochloric are added and the solution allowed to cool. The nails are then extracted and washed with cold water, about 2 cc. of starch indicator added and the solution titrated with the iodine solution until a final drop produces a permanent blue tinge.

48. In the assay for tin, half a gram of ore or concentrate is taken, or 1 gram of tailings or slag. The charge is placed in a thin iron crucible of about two inches in height by two in diameter, moistened with a few drops of water and about four inches of stick caustic potash or caustic soda added, the crucible is covered and gently heated over a lamp for several minutes and finally at a high heat over a blast lamp until complete fusion; the melted contents are then poured out upon a clean iron plate and as soon as cooled are dissolved in water along with that which adheres to the crucible and cover. Hydrochloric acid is now added until the solution is neutralized, about 10 cc. excess and 8 to 10 nails or iron chain added and the assay finished as described in paragraph 47, taking the precaution to heat the solution containing the nails until it is completely discolored.

49. The only disturbing element is sulphur in the form of sulphide, *i. e.*, pyrite, galena, zinc blende, etc., in which case it is necessary to thoroughly decompose the material with nitric acid and chlorate of potash until the disappearance of all globules of free sulphur, by means of repeated evaporations to dryness. It is then cooled, 10 cc. of HCl added, boiled and the insoluble residue, containing all of the tin, is filtered off and washed, dried and fused in the iron crucible as described in the preceding paragraph. The crucible and nails or chain can be used repeatedly.

In this method, as in all others, it is advisable to make a blank assay in order to prove the absence of disturbing substances; in case a result is obtained it should be subtracted from each assay made.

ANALYSIS OF COPPER AND LEAD SLAGS.

50. The sample of slag should be chilled by granulation in water, this leaves it in a proper condition for easy decomposition.

51. SILICA, SiO_2. About 1 gram is finely pulverized in an agate mortar

and half a gram weighed for the analysis. This is treated in a small casserole with 6 drops of water and stirred with a glass rod having a flat end; the casserole is gently heated and 3 cc. of hydrochloric acid added and quickly stirred until all has become gelatinized. With the glass rod, the mass is then removed from the bottom of the casserole and left adhering to the sides, it is then evaporated at a mild heat until the bulk of the moisture is expelled and is then pushed down and spread over the bottom and evaporated to complete dryness, but without heating it to the extent of oxidizing all of the iron. All of the lumps should be crushed with the flat end of the glass rod so as to liberate all the excess acid and completely dehydrate the silica. The casserole is now cooled, covered and about 10 cc. of HCl added, it is then boiled, about 40 cc. hot water added and filtered, washing well with hot water and a few drops of HCl which are dropped around the edge of the filter paper. The filter is then dried, ignited and weighed as SiO_2, deducting the weight of the filter paper ash.

52. ALUMINA, Al_2O_3. To the filtrate from the silica, 3 cc. of nitric acid are added and the solution boiled to oxidize the iron, an excess of ammonia is added, the solution gently boiled, filtered and washed with hot water and ammonia several times. The filtrate is set aside for the determination of Magnesia. The precipitate is dissolved through the filter by means of hot diluted hydrochloric acid, again precipitated with ammonia, boiled, filtered, washed as before, dried, ignited at a low temperature and weighed as Al_2O_3 plus Fe_2O_3.

53. After determining the iron as described in paragraph 55, its weight is multiplied by 1.43, obtaining thus its equivalent in Fe_2O_3, and this weight deducted from the combined weight obtained in the preceding paragraph leaves the weight of the Al_2O_3 desired.

54. MAGNESIA, MgO. To the two filtrates, combined, mentioned in paragraph 52, is added 3 grams of oxalate of ammonia, the solution is boiled about 15 minutes to collect the calcium oxalate and is then settled, filtered and washed with hot water and ammonium chloride; in case that the slag contains much magnesia, say over 5 per cent., the precipitate should be redissolved in hydrochloric acid, the lime reprecipitated with ammonia and ammonium oxalate, filtered, washed as before, and the combined filtrates treated as already described in paragraph 25.

55. IRON, Fe. Half a gram of the sample is placed in a beaker with about 50 cc. of hot water, boiled, and while being stirred with a rod 15 cc. of HCl are added, the solution boiled for about three minutes, about 50 cc. hot water and 10 grams of granulated lead are added and the boiling continued at a gentle heat until the solution is completelydiscolored and all copper precipitated; the solution is then cooled, about 5 cc. of HCl added, the clear solution decanted, the lead washed three times with cold water, the decantations added to the main solution which is then titrated with bi-chromate of potash as described in paragraph 12.

58. LIME, CaO. Half a gram of the sample is treated in an 8-ounce beaker with 30 cc. of hot water; while boiling it is stirred and exactly 5 cc. of nitric acid added, the boiling continued about two minutes, when 100 cc. more of boiling water are added. If the sample has been properly chilled it will be found that all has gone into solution. The silica will remain in solution as long as it is kept hot and diluted. A drop or two of sulphuric acid is now added to precipitate any barium present, as sulphate. While boiling and stirring, ammonia is now

added, drop by drop, until all free acid is neutralized, but not sufficient to precipitate any of the iron. An indication of the proper stage is given by the solution turning red and possibly a few flakes of gelatinous silica will appear. Should much silica be precipitated, it will be necessary to begin over again with a new charge and add the ammonia more cautiously. As soon as the red color has appeared, 3 grams of oxalate of ammonia are added, the beaker covered and boiled vigorously for about five minutes. The lime precipitates as oxalate in a granular condition and filters readily. It is now filtered, washed twice with hot water, twice with ammonia and hot water and twice again with hot water. The precipitate is now treated as described in paragraph 30. (The Author, Eng. & Min. Jour., February 10, 1900.)

59. ZINC, Zn. In a porcelain casserole half a gram is moistened with 3 drops of water, stirred, 5 cc. of nitric acid added and evaporated almost to dryness, half a gram of chlorate of potash and 5 cc. more of nitric acid are added and the whole evaporated to complete dryness. The casserole is cooled, 3 grams of ammonium chloride, 50 cc. water and 10 cc. ammonia are added and stirred, it is then boiled, filtered and washed four times with hot water containing ammonium chloride and ammonia.

60. The filtrate is neutralized with hydrochloric acid and 5 cc. excess added, about 5 grams of granulated lead added and it is then boiled until all copper is precipitated, 5 cc. more of hydrochloric acid added and titrated hot with ferro-cyanide of potash.

61. The solution of ferro-cyanide is added little by little from a burette, stirring vigorously after each addition and testing a drop of the solution for assay with a drop of a saturated solution of uranium acetate on a porcelain drop plate, the assay is finished when the uranium acetate gives a slight red color. In order to avoid an excess of the titrating solution, it is well to reserve a part of the assay solution and add it to the main solution after the end point has been reached.

63. The standard solution of ferro-cyanide of potash is made by dissolving 39.78 grams of the salt in hot water and diluting it to a volume of 1 litre; 1 cc. equals about 5 miligrams of zinc or 1 per cent. on a half gram charge.

64. To standardize the solution, 200 miligrams of metallic zinc or 250 miligrams of zinc oxide (which contains 200 miligrams of zinc), are dissolved in 5 cc. hydrochloric acid, about 4 grams of ammonium chloride added, diluted with 50 cc. hot water and titrated as before. Before finishing the titration, when there lacks 2 or 3 cc. of the end point, the solution for assay is diluted to a volume of 150 cc. and the titration completed. The assay of the slag should be completed at the same volume likewise. A blank assay should be made, using the same quantity of reagents as in the actual assay, and the result thus obtained should be deducted from the burette reading of both the standard and the assay; this generally amounts to about 0.3 of 1 cc.

65. MANGANESE, Mn. (Volhard's Method.) One-half gram of the sample is placed in a large beaker or half-litre flask, 50 cc. of hot water added, boiled, and while being agitated, about 10 cc. of hydrochloric acid are added and boiled about two minutes; half a gram of chlorate of potash is then added and again boiled until all odor of free chlorine has been expelled. About 150 cc. of hot water and 3 cc. of the same acid added and again boiled and about 30 grams of zinc oxide made into an emulsion are gradually added and the whole

maintained at the boiling point while titrating with the same solution of permanganate of potash as that used in the lime determination, agitating vigorously after each addition of permanganate until the end point is reached. The end is indicated by a faint pink tinge which persists even after a minute of boiling. (See paragraph 33.)

66. COPPER, Cu. (Eng. & Min. Jour., Dec. 25, 1909.) Five grams of the thoroughly chilled and finely ground sample of slag is treated in a large beaker of about 600 cc. capacity; 200 to 400 cc. of hot water added, boiled and while boiling, 15 cc. sulphuric acid previously diluted in cold water are added gradually with stirring to prevent the slag from adhering to the bottom of the beaker. The entire slag goes into solution almost immediately with the exception of matte, metallic copper, sulphates of lead, barium and lime, and undecomposed carbon. The latter forms a slight scum on the surface of the solution but in no way interferes with the assay. About six large strips of sheet aluminium are added and the solution gently boiled for about twenty minutes or until the aluminium appears clean and the precipated copper detached from it. The solution and precipitate are now transferred to another large beaker, leaving behind the strips of aluminium, which are washed free from copper and the washings added to the main solution which is allowed to settle and then decanted; about 200 cc. of hot water are added to the precipitate, which is again allowed to settle and the solution decanted.

67. The residue containing the precipitated copper, undecomposed matte and shot copper is now dissolved in nitric acid and the copper determined by the cyanide, iodide or electrolytic methods as described in paragraphs 38, 43 or 84.

68. In order to retain the silicates in solution and prevent the precipitation of gelatinous silica, the solution should have considerable volume and be kept dilute and hot. Too much acid will dehydrate it.

69. If the titrating solutions of potassium cyanide or iodide are of a strength that 1 cc. is equivalent to 5 miligrams of copper, then on a 5 gram charge, 1/10th cc. is equivalent to 1/100%, which is delicate enough for practical purposes.

71. LEAD, Pb. The slag is decomposed as described in paragraph 66, diluted to a large volume with hot water and the sulphate of lead and residue allowed to settle about ten minutes, the solution is then decanted and the settled residue dissolved in 5 cc. nitric acid and 10 cc. sulphuric acid, evaporated at a strong heat until copious white fumes are evolved. After cooling it is diluted with about 30 cc. cold water, boiled, filtered and washed several times with hot water.

72. The filter paper and precipitate is placed in a beaker and boiled with about 30 cc. of a concentrated neutral solution of ammonium acetate; diluted with hot water and titrated with molybdate of ammonia, using a solution of tannin on a drop-plate as indicator of end reaction. The molybdate solution is prepared by dissolving 8.72 grams of the salt in hot water and diluting to two litres; 1 cc. precipitates about 5 miligrams of lead or 0.1 per cent. on 5 grams of initial charge. The strength of the tannin solution is about 0.2 grams to 100 cc. water.

73. To titrate the molybdate solution, about ½ gram of pure sulphate of lead is ground very fine in an agate mortar, exactly 293 miligrams are weighed,

dissolved in 30 cc. of ammonium acetate, diluted to about 200 cc. with hot water and titrated hot. To avoid over-running the end point, a portion of the solution of lead is reserved and added, after the main portion has been titrated and the end point reached; 293 miligrams of sulphate of lead is equivalent to 200 miligrams of lead.

LEAD, Pb. (In Ores, etc.)

74. (Alexander's Method.) The solutions of ammonium molybdate and tannin are described in paragraph 72, and the titration in paragraph 73.

76. In the assay of ores, etc., half a gram is decomposed as described in paragraphs 39 and 40. After cooling, about 100 cc. of water are added, boiled, filtered and washed several times with hot water and dilute sulphuric acid and the precipitate dissolved and titrated as in paragraph 72.

77. Interfering elements are lime and bismuth. To eliminate them, the precipitate of lead sulphate is dissolved in ammonium acetate and the lead reprecipitated by adding dilute sulphuric acid, boiling, filtering, washing and titrating as before.

SULPHUR, S.

78. Half a gram of the sample is treated in a casserole with 10 cc. of water and an equal quantity of HNO_3 heated gently until the first violent action has ceased, 2 grams of chlorate of potash added and the whole evaporated to dryness, but without baking.

79. After cooling, 5 cc. of HCl and 30 cc. of water are added, boiled, filtered and the residue washed with hot water. To the solution is added 2 grams of barium chloride previously dissolved in hot water, the mixture is boiled vigorously for half an hour, during which operation the evaporated water should be replaced. Finally 5 cc. of HCl and 300 cc. water are added, boiled, allowed to settle, filtered, washed with hot water and a few drops of HCl, after which the residue is dried, burnt and weighed as $BaSO_4$, which weight multiplied by 0.275, gives percentage of sulphur.

80. To determine the sulphur existing in the form of sulphate, ½ a gram of the sample is simply dissolved in 5 cc. of HCl and 30 cc. of water, boiled, filtered, washed and the sulphur precipitated in the filtrate with a solution of barium chloride. The contents of the beaker are then boiled for about 20 minutes, filtered, washed and the precipitate weighed as usual, as $BaSO_4$. This result deducted from that obtained as per paragraph 79 leaves the sulphur existing as sulphides.

81. In the above methods sulphur as barium sulphate in the ore does not score and this is an advantage in some smelting plants where it is desired to obtain the sulphur as sulphide only. If the total sulphur is required, half a gram of the sample is fused in an iron crucible with a mixture of sodium carbonate and chlorate of potash, the fused mixture is dissolved in hot water and filtered. To the solution is added HCl until slightly in excess, 2 grams of barium chloride added to precipitate the total sulphur as barium sulphate which is then determined as before.

ZINC, Zn.

82. Half a gram of the sample is decomposed as described in paragraph 78 and heated gently until no odor of acid is left, cooled, 5 grams ammonium chloride and 10 cc. ammonia added and the mass stirred to loosen it from the casserole, 30 cc. water are added and after bringing to a boil the residue is fil-

tered off and washed several times with hot water and ammonia. From 5 to 15 grams of granulated lead are now added to the solution, according to the amount of copper present in it as indicated by the intensity of the blue color. The solution is then neutralized with HCl and 5 cc. added in excess, is gently boiled until all copper is precipitated as will be indicated by the solution becoming colorless, 5 cc. HCl are added and the solution titrated as described in paragraphs 60 to 64.

COPPER BY ELECTROLYSIS.

83. Half a gram of sample is dissolved in 7 cc. water and 5 cc. $HN0_3$, and should there be much sulphide present, as would be indicated by violent action, ½ gram of chlorate of potash is added and the whole evaporated to dryness. After cooling, 2 cc. HNO_3 and 10 cc. of water are added and boiled. If the sample contains no disturbing elements, as silver, arsenic, antimony, and lead, proceed as follows:

84. The solution is neutralized with ammonia, 2 cc. H_2SO_4 added, and the solution diluted to a volume of about 80 cc. after transferring to a beaker about 3½ inches high by 1¾ inches in diameter. A platinum cylinder about 2½ inches high by 1½ inches diameter is hung in the beaker and inside of the cylinder, but without touching it, is hung a spiral of platinum wire. Two gravity battery cells are connected with it, the zinc pole being attached to the platinum cylinder cathode. (Where a great many determinations are to be made regularly the depositions are generally made during the night and advantage taken of the electric lighting current.) The current is allowed to flow during a night and next morning 10 cc. of water are added to raise the level on the cylinder wire which has no deposit of copper; if after twenty minutes no copper is deposited on the bright wire, it is indication that all has been deposited. Another way of testing, is to take out a few drops of the solution and bring them into contact with H_2S. The ammonia test is not delicate enough.

85. The beaker is now lowered away from the hanging cylinder and spiral and another filled with pure water quickly put into its place without interrupting the current. (A convenient procedure is to place the beaker containing the solution, cylinder, etc., on a block of wood 4 inches high, which can be drawn away in order to lower the beaker readily and make the exchange before the deposited copper can redissolve.) The second beaker is now removed, the cylinder loosened and washed in water then in alcohol and carefully dried so as to not oxidize the thin film of copper. It is then weighed, the copper dissolved off in nitric acid, again washed in water, alcohol and weighed, the difference in weight representing metallic copper.

86. The use of a cylinder and beaker avoids the necessity of filtering the solution before precipitation, but this must be done in case of using a platinum dish instead of the cylinder as cathode.

87. Disturbing elements are, silver, arsenic, antimony and lead. To eliminate the silver it is precipitated with a minimum quantity of salt solution before the deposition of the copper, as an excess forms free chlorine with the nitric acid and dissolves the platinum spiral and may deposit platinum on the cathode with the copper. It is not necessary to filter off the silver chloride unless the intention is to effect the precipitation in a dish.

88. To eliminate arsenic and antimony, 4 cc. of H_2SO_4 are added after decomposition of the sample with nitric acid and chlorate of potash. It is then

evaporated to white fumes and cooled. Ten cc. of water, 5 cc. of HCl and ½ gram of bisulphite or sulphite of soda or ammonia are added and the whole again evaporated to white fumes. In this operation all arsenic and the greater part of the antimony is volatilized and in repeating the evaporation with another 5 cc. HCl, the balance of the antimony will be eliminated.

89. A small amount of lead does not interfere, but if an appreciable quantity is present in the sample, it is eliminated by filtering off the sulphate after evaporating to white fumes with sulphuric acid and diluting with water.

TUNGSTEN, W.

90. Almost all of the tungsten ores decompose in aqua regia and the determination of WO_3 in such ores is extremely simple. The insoluble residue is determined on two initial charges of the sample, as described in paragraph No. 1. Upon filtering the two residues, one is washed with hot water and ammonia, the other is washed with hot water only, the difference in weight between the two residues is WO_3, which has been dissolved by the ammonia. This weight multiplied by 0.793 will give the equivalent in W.

91. Those ores which do not decompose in aqua regia must be decomposed in hydrofluoric acid. One half gram of the sample is treated in a platinum dish with 5 cc. of HCl and 5 cc of HF and evaporated almost to dryness, the same acids are again added and again evaporated, this time to complete dryness, 5 cc. of HCl are added and the contents transferred to a beaker with hot water, 5 cc. nitric acid are added, the solution boiled until the yellow precipitate of WO_3 is in a granular form, it is then filtered and washed with hot water and a few drops of HCl, dried, burnt and weighed. This weight represents insoluble residue, WO_3, and perhaps chloride of silver and stannic oxide. The residue is transferred to a beaker and boiled with aqua regia and water, and again filtered and washed with hot water and HCl, finally it is washed with ammonia and hot water to dissolve WO_3 and dried and burnt as before, then weighed as insolube residue, the difference between this weight and the former one being WO_3 plus AgCl.

92. Silver is an interfering element, but is seldom found in tungsten ores. To eliminate it, the best method is to make a silver assay which, multiplied by 1.328, will give the equivalent in AgCl, which is then deducted from the last result above.

ARSENIC, As, AND ANTIMONY, Sb.

93. In the metallurgy of gold, silver, copper, lead and tin, arsenic and antimony are considered as impurities and it generally suffices to determine them combined; for this, 1 gram of the substance is decomposed as described in paragraph 78; after cooling, 10 cc. of HCl and ½ gram of tartaric acid are added, boiled, diluted to about 150 cc. with hot water and a current of H_2S gas is run in until all sulphides are precipitated, the precipitate is allowed to settle in a warm place and then filtered, washing with hot water; the funnel containing the filter and precipitate is then inverted over a beaker and the bulk of the precipitate transferred to the beaker by means of a stream of water and without removing the filter from the funnel; the solution in the beaker is made up to about 50 cc. with hot water and 2 grams of caustic potash or soda are added to dissolve the sulphides of arsenic and antimony; the contents of the beaker are boiled, filtered through the same filter as before and washed with hot

water and a few drops of caustic potash until all yellow precipitate is dissolved from the filter. Two grams of chlorate of potash are added, the solution boiled and during the boiling HCl is added little by little until the solution is neutralized, 10 cc. in excess are then added and the boiling continued until all of the free chlorine is expelled and any globules of sulphur decomposed. After adding ½ a gram of tartaric acid the solution is filtered and washed, diluted to a volume of about 400 cc. and the sulphides again precipitated with sulphuretted hydrogen, the precipitate allowed to settle in a warm place for several hours. The clear supernatent liquid is decanted into a large beaker together with any floating precipitate and it as well as the settled precipitates are diluted to as great a volume as possible with hot water and again settled; after a few hours the supernatent liquid in both beakers is decanted and thrown away, no note being taken of a few floating specks. The precipitates are then transferred to a Gooch crucible, previously prepared and weighed with a thin filter of asbestos fibre, and attached to a suction apparatus.

94. The precipitates are washed twice with hot water and once with pure alcohol to displace the water, the washings are then thrown away and the Gooch crucible disconnected from the suction apparatus and the precipitate washed once with bisulphide of carbon to dissolve any free sulphur which may be present, attached again to the aspirating apparatus in order to draw out the bisulphide, washed again with alcohol, dried at a temperature not exceeding 125° C. to a constant weight which represents As_2S_3 plus Sb_2S_5 and this multiplied by 0.6 gives As plus Sb.

ARSENIC (By Distillation.)

95. (Fischer's Method.) The most rapid and exact method is by distillation, a method little known and somewhat difficult at first, but well worth practicing if the chemist may have many assays to make.

96. A solution of iodine is prepared by dissolving 3.36 grams of metallic iodine and 6 grams of iodide of potash in 20 cc. of hot water and then diluting up to 1 litre with cold water. One cc. is equivalent to about 1 miligram of arsenic or one-tenth of a per cent. on 1 gram. (One cc. is also equivalent to 1.6 miligrams of antimony.)

97. To titrate it, 132 miligrams of arsenious acid, As_2O_3 (equivalent to 100 miligrams of As.) are dissolved in about 20 cc. of hot water and 1 gram of caustic potash, 100 cc. of cold water added, neutralized carefully with HCl in which there should be only 1 or 2 drops in excess, 5 grams of bicarbonate of soda are added, cooled, a few drops of starch solution are added and the solution titrated with the iodine solution until the appearance of a faint blue color.

98. In the analysis, 1 gram of the sample is decomposed as in paragraph 40, if a sulphide, or as in paragraph 39 if an oxide, 30 cc. of water are added, boiled, filtered and washed with hot water, evaporated to a volume of about 30 cc. and transferred to a distilling flask of about 150 cc. capacity, which has a rubber stopper with 2 perforations in one of which is a bent glass tube connecting with a condenser and in the other is a separatory funnel.

99. The Allihn condenser is a convenient one, or one may be made by bending a tube in the form of a "U" and expanding the bend by blowing so as to form 3 bulbs of about 2 inches diameter, the latter form may also be purchased. To effect the condensation of the distillate, enough cold water is added to fill 1 of the bulbs, or in the case of using an Allihn or other form of condenser the tip

of the outlet tube is barely immersed in a beaker containing about 30 cc. of water.

100. To effect the distillation, about 1 gram of *ferrous*-sulphate and 10 cc. of HCl are added to the flask and after making tight connections with the condenser, the contents are gently boiled over a flame until the bulk of the solution has been evaporated and the remaining contents show a tendency to jump. The beaker which receives the condensed distillate is quickly removed and then the flame. In case of reversing this order, the flask cools and draws up the contents of the beaker. Five cc. more HCl are added to the flask, the beaker replaced under the condenser, the tip of the outlet tube being barely immersed as before, the flame again applied until bumping again occurs when the beaker containing the distillate is again removed, and then the flame withdrawn. In this operation the arsenic is reduced by the ferrous-sulphate to arsenious chloride which is volatile even at a temperature below the boiling point of water. The distillate now contains all the arsenic as well as the HCl and this latter is now neutralized with ammonia, then HCl cautiously added until only 1 or 2 drops in excess, 5 grams of bicarbonate of soda added and the titration finished as described in paragraph 97.

101. There are no interfering elements, but it is necessary to observe the precaution of eliminating all nitrates and sulphurous acid by following directions as given in paragraph 39.

ANTIMONY, Sb.

102. Referring to paragraph 100, the residue left in the flask after finishing the distillation of the arsenic, still contains the antimony which is dissolved in 10 cc. HCl and ½ a gram of tartaric acid and after diluting and precipitating with H_2S, is determined as described in paragraphs 93 and 94; in this case the result is antimony alone.

ARSENIC AND ANTIMONY.

103. The following method determines arsenic and antimony by fractional distillation in any cupriferous substance as ores, pyrites, matte, precipitates, blister or refined copper. (E. & M. Jour., Dec. 16, 1899, and Jour. Soc. Chem. Ind., March 30, 1901.)

104. Any quantity of substance is weighed out, for example; 1 gram of ore, matte, or precipitate, 10 grams of blister or 100 grams of refined copper, and is dissolved in a minimum quantity of nitric acid, chlorate of potash being added if necessary to oxidize all sulphur. If the substance does not contain iron, about 100 miligrams are added in solution, the volume is made up to about 300 cc., boiled and bicarbonate of soda, in powder form, is added until a white precipitate is formed; should a little of the iron be precipitated it makes no difference. This precipitate contains all of the arsenic and antimony.

105. It is allowed to settle in a warm place and then filtered and washed with hot water. The funnel is then placed in a distilling flask and the precipitate dissolved through the filter with about 20 cc. of HCl and hot water. The funnel is then removed with filter and residue which is discarded. To the flask is added 25 cc. of a saturated viscous solution of zinc chloride, made by dissolving metallic or oxide of zinc in HCl and evaporating to a consistency of syrup, also 5 grams of cupric chloride and about 200 miligrams of pure copper foil are added to the flask which should have a rubber stopper with three perforations;

in one is a glass tube connected with a condenser, in another is a thermometer reading up to 200° C., and in the third is a separatory funnel terminating in a fine point which is slightly bent away from the thermometer so that the acid which is introduced may not fall upon it.

106. The flask is now attached to the condenser, a beaker containing about 30 cc. of water is placed under the condenser to catch the distillate, and the flask is gently heated, care being taken that the temperature does not exceed 115° C. After about 10 minutes boiling, the temperature is allowed to rise to 115° and as soon as this is reached, the beaker containing the distillate is removed and set aside for determining the arsenic; another beaker with water is placed under the condenser to collect the antimony, which still remains in the flask.

107. The antimony, in form of antimonious chloride, does not distill over until the temperature is much superior to 115°. The flask is again heated until the temperature reaches 150° when 10 cc. of HCl are placed in the separatory funnel and allowed to flow very slowly into the flask and without removing the lamp or flame; the acid should vaporize as it leaves the point of the funnel so that no liquid acid falls upon the melted mass in the bottom of the flask nor upon the thermometer. As the beaker for collecting the distillate fills with solution, it must be constantly lowered so that only the tip of the outlet tube touches the surface of the water, otherwise a sudden cooling, however slight, of the flask, will cause the water of the beaker to be drawn up through the condenser into the flask and crack it, or even explode. As soon as the 10 cc. of HCl have entered the flask, the funnel is closed and the temperature raised gradually to about 200° C. when all of the antimony will have been vaporized and condensed in the distillate. The funnel is now opened, the distillate removed and then the lamp removed last of all.

108. The antimony distillate is now neutralized with ammonia, first adding about ½ gram of tartaric acid to the distillate; it is then made slightly acid with HCl, having only about 1 or 2 drops in excess, 5 grams of bicarbonate of soda are added, allowed to cool, a few drops of starch solution added and then titrated with the iodine solution mentioned in paragraph 96.

109. The arsenic distillate mentioned in paragraph 106 is neutralized with ammonia, 1 or 2 drops of HCl in excess added, 5 grams of bicarbonate of soda added, cooled, starch added and titrated as before.

110. The method may be used for determining arsenic and antimony in almost any substance beside those already mentioned, as for instance, beer, wine, organic matter and even a stomach. The liquors are evaporated to a small volume and then the organic matter as well as the As and Sb are oxidized by nitric acid and after the first violent action has ceased, chlorate of potash is added and thorough decomposition obtained before adding the bicarbonate of soda to precipitate As and Sb. In substances containing much lead, it is advisable to expel the nitric acid by boiling to white fumes with sulphuric acid and then filtering off the lead sulphate before precipitating with the bicarbonate of soda.

111. About the only element which interferes is selenium, which occurs generally together with tellurium in electrolytes, or rather in the residue from the electrolytes in copper refineries. In the distillation method, selenium distills over with the antimony and immediately precipitates in the distillate forming a dainty pink colored deposit which must be settled and filtered off before determining the antimony.

CHLORINE, Cl.

112. The oxichloride of copper (Atacamite) is volatile and in smelting it, a great part escapes through the chimney of the furnace. In order to penalize it in purchasing ores, many smelting works make the assay for copper after first calcining the weighed portion, the Atacamite being thus eliminated. Said method leaves much to be desired and the following is more exact:

113. The following solutions are required:

Nitrate of silver; 4.791 grams are dissolved in 1 liter of water. If the crystals are pure and dry when weighed, 1 cc. of the solution will precipitate 1 miligram of chlorine, and the solution need not be standardized against pure salt.

Chromate of potash; About 1 gram is dissolved in 200 cc. water.

Caustic potash; About 100 grams to a liter of water.

Nitric acid; 200 cc. of concentrated acid diluted to 1 liter.

114. As it is impossible to obtain reagents completely free from chlorine, a blank assay is made upon exact measures of these reagents and then the same measures are employed in the actual assay of ore, etc. For this purpose 10 cc. exactly, of the caustic solution are taken, and from a burette is added the nitric acid solution until neutral, using litmus paper as indicator. The caustic solution is again added drop by drop until the paper turns blue, but there should be not more than 2 drops of caustic in excess. A few drops of the chromate solution are now added, the volume is made up to 100 cc. with cold water, and is then titrated with the silver nitrate solution until a faint but permanent red color appears. The quantity of silver nitrate consumed thus represents the quantity of chlorine in the reagents and must be deducted from the standard and from each assay.

115. If necessary at any time to standardize the silver nitrate, 82.4 miligrams of pure salt, which is equivalent to 50 miligrams of chlorine, are dissolved in 10 cc. of the caustic solution, neutralized as described in the last chapter and titrated.

116. In the assay of ores, etc., 1 gram of the sample is treated with 10 cc. of the caustic solution and boiled gently about 5 minutes, about 10 cc. of pure hot water are added and the same quantity exactly of the nitric acid which was used in the blank assay is likewise added; litmus paper is introduced and the caustic solution added drop by drop until the paper barely turns blue. The mixture is then boiled about 2 minutes, filtered through a paper free from chlorine, washed with hot water, chromate of potash added, the volume made up to 100 cc. with cold water and then titrated with the silver nitrate, deducting from the result the amount of nitrate solution consumed in the blank test. One cc. of nitrate of silver solution is equivalent to one-tenth per cent. of chlorine.

117. The use of nitric acid as a solvent is not to be recommended, as it dissolves the copper and forms aqua regia with the chlorides present, hence the chlorine is expelled as free chlorine. The caustic solution decomposes Atacamite without dissolving the copper or expelling the chlorine.

(Note: The method for chlorine would have little application in the northern hemisphere, but it must be remembered that all these methods were originally written in Spanish for the National Mining Association of Chili, in which country exist vast deposits of Atacamite ores.)

BISMUTH, Bi.

118. Half a gram of the sample is decomposed as described in paragraphs

39 and 40, water added, boiled, filtered and washed with hot water and dilute sulphuric acid. The sulphides are precipitated from the filtrate by means of H_2S, warmed, filtered, washed with water containing H_2S and transferred to a clean beaker by means of a stream of hot water from a wash bottle and without removing the filter paper from the funnel. The sulphides of arsenic and antimony are dissolved with caustic potash as described in paragraph 93 and filtered through the same filter as before, washing with hot water and a little caustic.

119. The sulphide of bismuth, with other heavy sulphides, is dissolved through the filter paper into a clean beaker, by means of dilute nitric acid. The filtrate is almost neutralized with ammonia, not sufficient being added to produce a precipitate, the bismuth is then precipitated with carbonate of ammonia in excess, heated without boiling for some 20 minutes. If the solution contains no copper, as will be shown by the familiar blue color, the bismuth may be filtered immediately on a "Gooch" crucible, washed with hot water and ammonia, dried, burnt and weighed as Bi_2O_3 which multiplied by 0.897 gives Bi. If the solution contains much copper, the precipitate is filtered on an ordinary filter paper, washed with hot water and ammonia, the washings thrown away and the precipitate redissolved and reprecipitated as before and finally filtered on the Gooch crucible for final weighing.

NICKEL, Ni, AND COBALT, Co.

120. Half a gram of sample is decomposed as described in paragraph 78, cooled, 20 cc. of ammonia and 20 cc. of water added, the mass loosened from the bottom of the casserole by means of a glass rod, boiled a few minutes, filtered and washed with hot water and ammonia. The precipitate is redissolved in dilute sulphuric acid, reprecipitated with ammonia, filtered, washed with hot water and ammonia and the filtrate added to the first filtrate. The combined filtrates are boiled to expel the greater part of the ammonia, dilute sulphuric acid added in slight excess and the heavy metals precipitated with H_2S which are filtered off and washed with hot water containing H_2S. The filtrate is boiled to reduce its volume to about 80 cc. and at the same time expel the excess of H_2S, 50 cc. of strong ammonia is added and metallic nickel and cobalt precipitated by electrolysis as described in paragraph 84.

121. To separate the two elements, the deposit on the cylinder is dissolved in dilute nitric acid, evaporated to complete dryness and then redissolved in potassium cyanide, being warmed in a closed hood for a considerable length of time in order to expel all free cyanide. About 2 grams of very finely powdered red oxide of mercury is added to precipitate the nickel, the mixture is diluted with water, boiled, filtered and washed with hot water, the residue being then dried, burnt and weighed as NiO. This weight multiplied by 0.786 gives the equivalent of Ni. and the percentage of cobalt is then obtained by difference. If it is desired to check the nickel assay, the precipitate of NiO may be dissolved in sulphuric acid, diluted with water, 50 cc. of strong ammonia added and the nickel precipitated by electrolysis.

122. Naturally, the sample may possibly contain but one of these elements and if it is desired to verify the first precipitate of the electrolysis mentioned in paragraph 120, it may be dissolved in nitric acid and an excess of caustic potash added. Cobalt would give a blue precipitate which soon changes to black. Nickel would give an apple-green precipitate.

PHOSPHORUS, P.

123. A molybdate mixture is made as follows: 50 grams of molybdic acid is mixed with 100 cc. of water and then 100 cc. of strong ammonia are added with stirring; as soon as it is dissolved it is poured into a large beaker containing 250 cc. of nitric acid and 500 cc. of water mixed, allowed to settle for 24 hours and the supernatent liquid decanted off for use, being kept in a stoppered bottle.

124. To determine P. in ores, etc., ½ gram of the sample is dissolved in 20 cc. of HCl and evaporated to dryness, 20 cc. of nitric acid added, evaporated to a volume of about 10 cc., then 10 cc. of hot water are added and the residue filtered off and washed with hot water, the filtrate being received in a flask. The volume is now reduced by evaporation to about 30 cc., the temperature is lowered to 80° C., 30 cc. of the molybdate mixture are heated to the same temperature and added to the flask which is corked tightly, wrapped in a towel or cloth previously heated and the flask is then shaken for 5 minutes, allowed to settle 20 minutes, always at a temperature as close to 80° C. as possible, decanted and the precipitate transferred to a "Gooch" crucible by means of a stream of hot water containing 3% of nitric acid, the precipitate is washed several times with the same dilute acid to dissolve out all of the iron, then washed with hot water alone and finally with alcohol, dried at a temperature of 110° C. and weighed as $(NH_4)_3$ 12 MoO_3PO_4 which contains 1.654% of P.

125. As a check on the result, the precipitate of ammonium phosphomolybdate is dissolved in ammonia, filtered and washed with hot dilute ammonia; 5 cc. of magnesia mixture (see below) are added and after cooling is mixed with 100 cc. of ammonia as described in paragraph 25 and the determination is finished as in the said paragraph, omitting of course the addition of phosphate of soda and ammonia. The weight of the $Mg_2P_2O_7$ thus obtained, multiplied by 0.279 gives P.

126. The magnesia mixture is made by dissolving 10 grams of ammonium chloride and 30 grams of magnesium chloride in water, adding 20 cc. of ammonia, diluting to 500 cc., mixing, allowing to settle for 24 hours and decanting off the clear solution for use.

MERCURY, Hg.

127. (Eschka's method, modified.) The following apparatus is prepared; A weighed sheet of gold or silver foil is fitted over the bottom and around the sides of a porcelain or nickel crucible having a height of about 3 cms. and a diameter of about 4½ cms. This crucible, covered with the foil, is inserted as a cover into the top of another crucible of about 4 cms. height and 3½ diameter. The foil should be of a size large enough to reach about 1 cm. above the edge of the lower crucible so that it may be turned downward on the outside of the edge of the lower crucible, thus forming a well fitted top. A round hole is now made in the center of a piece of thick asbestos about 6 inches square, the hole should be about 3 cms. diameter so that the lower crucible, when placed in it, will project half below and half above the sheet of asbestos. This latter is placed on a tripod so that a Bunsen burner may be placed under it.

128. In making the assay, the foil is weighed and put into place after placing the charge in the lower crucible. The charge consists of ½ gram of the sample mixed with about an equal weight of pulverized chalk and about 2 grams of fine iron filings which pass an eighty mesh screen. The upper crucible is

filled with water to keep the foil cool and a couple drops of water are placed between the foil and bottom of the upper crucible to make good contact between them. The lamp is then placed under the sheet of asbestos containing the crucible and a gentle heat applied to the bottom of the lower crucible. This causes the mercury to distil and the fumes, on coming in contact with the gold or silver foil, condense and form amalgam. The water in the crucible forming the cover should be renewed occasionally with cold water. After about 10 minutes the heat is increased, care being taken to renew the water both inside and under the crucible cover, and after about 20 minutes all of the mercury should have been distilled and condensed on the foil. The foil is then cooled, washed with water, then with pure alcohol, dried and weighed, the increased weight being metallic mercury. This mercury is then expelled by heating at a high temperature, the foil is again weighed and is then ready for another use.

CADMIUM, Cd.

129. The solution of potassium ferro-cyanide mentioned in paragraph 63 is used. To standardize it, 100 miligrams of pure cadmium are weighed and titrated exactly as directed for the titration of zinc in said paragraph.

130. In the assay, half a gram of the sample is treated in a casserole with 10 cc. of water and 10 cc. of nitric acid. After the first violent action has ceased, 2 grams of chlorate of potash are added and evaporated to dryness. After cooling, about 4 grams of caustic potash and 30 cc. of water are added, the contents are boiled and filtered, the residue, containing the cadmium, is washed with hot water and a weak solution of caustic potash. The zinc in the filtrate may be determined as described in paragraph 60.

131. The precipitate is transferred to a beaker and boiled with 30 cc. of water, 10 cc. of ammonia and 2 grams of ammonium chloride, filtered, washed with hot water and ammonia and the cadmium determined as described in paragraph 60 for the determination of zinc, using, however, the standard obtained for cadmium as described in paragraph 129.

SILVER, Ag.

132. Ten grams of the sample are mixed in a clay crucible with about 40 grams of litharge and 30 grams of bicarbonate of soda. If the sample contains no sulphides, about 1½ grams of flour are added; if the sample contains much oxide of iron, about 3 grams of flour are added; but if the sample contains sulphides, the flour is replaced by nitre, the quantity varying with the quantity of sulphides present; for example, pure pyrites would require about 20 grams of nitre, an ore with an average amount of sulphides would require about 6 grams and an ore with only a small amount of sulphides would require neither nitre nor flour. After mixing the contents of the crucible they are covered with about 5 grams of borax glass and placed in the furnace or muffle, commencing the fusion with a gentle heat, gradually increasing it to a high temperature and allowing it to remain at this temperature about 5 minutes after all action has ceased in the crucible. The contents are then poured into an iron mould and, after cooling, the button of lead is separated from the slag. A convenient size of button is from 10 to 16 grams and if soft and free from speiss it is pounded on an anvil in order to free it from slag and is then cupelled. If the button is small, the assay should be repeated, varying the amount of flour or nitre in order to obtain a larger button; in this connection it is useful to bear in mind that 1

gram of flour reduces about 10 grams of lead, while 1 gram of nitre *prevents* the reduction of about 4 grams of lead. If the button is very large or contains speiss or copper, it is not pounded but is placed in a scorifier and enough granulated lead added to make a total, with the button, of about 30 grams, ½ gram of borax glass is added and the scorification concluded as described in paragraph 135, in this manner obtaining a pure lead button and of reduced size.

133. In the cupellation of the buttons, a convenient size of cupel is about ⅞ of an inch in height by 1¼ inches in diameter. In general, the cupel should weigh about 30% more, at least, than the button to be cupelled. The empty cupels are placed in rows in the muffle, a row of old cupels or false row of new ones is placed in front and all heated at a high temperature for about 20 minutes before introducing the lead buttons. After the buttons are placed in the cupels, the muffle door is closed until the buttons melt and their surfaces brighten, when the door is opened and the temperature lowered somewhat by placing empty crucibles behind the rows of cupels in the muffle. An idea of the proper temperature for cupellation can only be acquired by much practice, a thin ring of litharge feathers surrounding the resultant silver bead but at some distance from it, is the best indication that the temperature was not too high. The well known freezing takes place if the temperature is too low, in which case it is advisable to repeat the assay instead of losing time as well as silver in an attempt to thaw out the button. When the cupellation is almost finished, the crucibles are extracted, the muffle door closed and the temperature raised in order to eliminate the last traces of lead from the silver bead, after which the door of the muffle is again opened, the temperature lowered and the cupels moved little by little toward the front of the muffle so as to prevent spitting and consequent loss of silver. Finally the cupels are taken out, the beads extracted, cleaned and weighed, each miligram of weight represents one "Diez milesimo" (D.M.)of silver. It is advisable to make the assays in duplicate and the two beads resulting should correspond in weight.

134. The "Diez milesimo" (D.M.) has the following equivalents:

One one-hundredth of 1 per cent. (0.01%.)

2.917 troy ounces per ton of 2,000 lbs.

3.215 troy ounces per ton of 1,000 kilograms (or metric ton.)

3.267 troy ounces per ton of 2,240 lbs. (Long ton.)

135. The scorification method should be used in the assay of matte and cupriferous ores. Four charges of 2½ grams each are weighed, mixed in scorifiers with about 30 grams of test lead, 30 grams more of lead and 1 gram of borax glass are placed on top and the scorifiers placed in a hot muffle, the door is closed and the temperature raised until the contents melt and the surfaces become brilliant as in the cupellation. The door is then opened and the temperatue lowered slightly. The scorification is allowed to continue until the surface is covered with slag, when the muffle door is closed and the temperature raised as high as possible in order to thoroughly liquify the slag before pouring the contents of the scorifiers into the moulds. The lead buttons are separated from the slag, placed in other scorifiers with enough granulated lead to bring up the total weight to about 30 grams and then re-scorified as before and the resultant buttons cupelled.

GOLD, Au.

136. About 5 cc. of pure sulphuric acid are boiled in a parting flask of about 1 ounce capacity, 1 or more of the silver beads, obtained from the silver assay,

are then dropped into the boiling acid and the boiling continued until all the silver is dissolved; the flask is cooled and the acid decanted off; the gold residue is washed with hot water, decanted and treated with about 10 cc. of dilute nitric acid (2 volumes of acid to 3 of water), boiled, the flask filled with hot water, decanted, again filled with hot water containing ammonia and is then inverted over a small porcelain annealing cup, the gold residue allowed to settle, the water decanted, the drops adhering to the cup are absorbed by a strip of blotting paper or filter paper, the cup and residue are then dried, burnt at a slightly reddish temperature in the muffle, the gold transferred to the pan of the gold balance and weighed. If silver beads corresponding to 10 grams of sample were dissolved, then each miligram of weight of gold corresponds to 10 C. Ms. (Cien milesimos) or 100 grams per metric ton, or 2.917 troy ounces per ton of 2,000 lbs.

137. The weight of the gold residue deducted from the weight of the silver bead gives the weight of the silver alone.

In case that the silver bead does not dissolve in the acid, it indicates that the bead contains more than 25% of gold, in which case it must be inquartated so as to effect the separation of the two metals. This is done by melting the bead with three times its weight of pure silver, by means of a blow pipe, or by adding besides the silver a sufficient quantity of granulated lead to effect cupellation in a muffle, after which the silver and gold are separated as before described.

SPECIAL ANALYSES.

SILVER BARS.

138. (Fire assay.) The sample is weighed in duplicate, 1 gram being taken. At the same time 1 gram of chemically pure silver is weighed up and to each of the three is added 5 grams (weighed) of pure lead foil and the three are cupelled side by side in a muffle at the highest possible temperature. The muffle is then cooled and the cupels drawn gradually toward the front so as to avoid spitting, and finally extracted altogether. Expert manipulation is required to avoid spitting. The silver beads are weighed and the loss of weight of the bead of pure silver is added to the weights of the other two, which, needless to say, should check each other closely. The gold is determined on the resulting beads as described in paragraph 136, using 15 cc. of acid.

139. (Wet method.) A standard solution of sulpho-cyanide of ammonium is prepared by dissolving 750 miligrams of the salt in 1 liter of water. 1 cc. of this solution precipitates about 1 miligram of silver. To standardize it, 50 miligrams of pure silver are dissolved in 5 cc. of nitric acid and 10 cc. of water, both free from chlorine, the red fumes are expelled by boiling, cold water added to bring up the volume to 100 cc., 5 cc. of ferric nitrate (made by dissolving about 5 grams of the salt in 200 cc. water) added, and then titrated until a faint pink but permanent end color is obtained.

140. Another solution is made by dissolving 12.6 grams of common salt in 1 liter of water. One cc. of this solution precipitates about 0.0199 grams of silver, and is standardized as follows: Exactly 2 grams of pure silver are dissolved in 10 cc. nitric acid and 20 cc. of water free from chlorine, the red fumes expelled by boiling, cooled and exactly 100 cc. of the salt solution added from a "Dafert" pipette. The solution of the silver is effected in a flask of 200 cc. capacity, which has been carefully calibrated with an ordinary 100 cc. pipette and has a scratch on the neck representing exactly 200.5 cc. After adding the

salt solution, the flask is tightly stoppered and shaken thoroughly, pure water added, bringing the volume up to the 200.5 cc. mark, again shaken and the precipitate allowed to settle; 100 cc. are now taken out, free from precipitate, by means of a pipette and after adding 5 cc. of the ferric nitrate solution are titrated with the solution of ammonium sulpho-cyanide. The quantity of sulpho-cyanide of ammonium used is multiplied by two and its equivalent in silver is deducted from 2 grams, the difference being the quantity of silver precipitated by 100 cc. of the salt solution. The concentration of the salt solution should be varied so that 100 cc. precipitates a little less than the fine contents of silver contained in 2 grams of the sample to be assayed, so that nearly all of it is precipitated by the salt, leaving only a very small amount of the silver still in solution so that the titration may be finished by the more delicate solution of sulpho-cyanide of ammonium.

141. In the actual assay of silver bars, 2 grams of the granulated sample are weighed up and treated exactly as described in the standardizing of the salt solution, finishing the titration with the solution of sulpho-cyanide of ammonium, side by side with the 2 grams of pure silver used for standardizing, so that the pink tinge at the end will have the same intensity in each case.

GOLD BARS.

142. Chemically pure gold is prepared as follows: About 10 grams of gold in any form are dissolved in aqua regia and the solution is boiled to expel all free chlorine, diluted to a volume of about 10 liters and allowed to settle for about one week. The clear liquid is decanted upon a filter by means of a syphon so that the settled residue may not be disturbed. About 2 pounds of pure oxalic acid are dissolved in water and mixed with the gold solution and allowed to stand for a week, the clear solution decanted off, the gold precipitate washed by decantation, twice with hot water, once with boiling dilute nitric acid, twice more with hot water, once with hot water and ammonia and finally with hot water. It is then dried and melted in a graphite crucible.

143. In the assay, the sample of gold bar is passed through rolls for the purpose of drawing it out into thin strips, observing strict cleanliness in this as well as all of the operations. Duplicate weights of ½ gram are taken and likewise ½ gram of the "proof gold," all being weighed on a delicate gold balance. To each of the three is added exactly 20 miligrams of pure copper, 1.25 grams of pure silver and 4 grams of pure lead foil. In a muffle, heated as hot as possible, are placed three cupels and after 20 minutes the three weighed charges are placed in them and cupelled at a high temperature, side by side. The resultant beads are rolled into thin strips, tempered in a muffle at a red heat and then treated in a parting flask for five minutes with nitric acid of 22° Baumé (three volumes water to one of acid), after decanting they are boiled for five minutes with acid of 32° B. (one volume acid to one of water), and again decanted and the gold is washed four times with hot water, dried, tempered in the muffle until the characteristic gold color is obtained, cooled and weighed; to the weight of the sample of gold bar is added the quantity of gold lost in the treatment of the pure or "proof gold." (This loss is about ½ miligram, generally.) The purity of the gold and also of bar silver is generally reported in fine parts per thousand, for instance, 99.85% would be reported as 998.5 fine.

BAR COPPER. (Complete Analysis.)

144. Gold and Silver. Twenty grams of the sample are placed in a large beaker of about 700 cc. capacity and treated with 150 cc. cold water and 55 cc. nitric acid. After the first violent action has ceased, 30 cc. more of nitric acid are added and later on more nitric is added if necessary to dissolve all of the copper. The solution is diluted with hot water to about ½ liter, allowed to settle for an hour and then filtered, washing the residue, which contains the gold, with hot water and a few drops of nitric acid. The filter is then folded and placed in a scorifier to be dried. In the filtrate the silver is precipitated by a minimum quantity of hydrochloric acid, or better still, if the approximate silver content is known, it may be precipitated by means of a slight excess of the salt solution mentioned in paragraph 140. The precipitate of silver chloride is stirred and allowed to settle over night, filtered, washed with hot water and nitric acid and the filter folded and added to the scorifier containing the gold residue. After drying, the filter papers are burnt with the addition of about 1 gram of litharge, then about 20 grams of test lead are added and the gold and silver determined as described in paragraph 135.

145. Copper. The filtrate obtained from the silver precipitate above, is diluted with cold water to exactly 1 liter, the liter flask having been carefully calibrated with a "Dafert" pipette of 25 cc. capacity. The solution is transferred to a large beaker and thoroughly mixed and 25 cc. are extracted by means of the same "Dafert" pipette (the interior of the pipette should *not* be washed out and added to the 25 cc. extracted for assay, as it is intended to deliver the necessary quantity and the liter flask should be calibrated to the delivery of the pipette.) The 25 cc. represent ½ gram of the original sample and is treated as described in paragraph 84 for determining copper by electrolysis. An additional 25 cc. is generally taken as a reserve portion.

146. Iron. From the remainder of the filtrate mentioned in the preceding paragraph, ½ liter, corresponding to 10 grams of the sample, is taken and neutralized with ammonia, a sufficient excess is then added to dissolve all of the copper hydrate, the solution boiled a couple of minutes, filtered, washed with hot water and ammonia, the precipitate redissolved in hydrochloric acid, reprecipitated with ammonia, filtered and washed as before, redissolved again in hydrochloric acid and the iron determined as described in paragraph 12.

147. Insoluble Residue. Six grams of the sample are placed in a flask with 6 grams of chlorate of potash and 30 cc. of hot water, 15 cc. of HCl are added little by little and, after about 15 minutes, 30 cc. more of HCl are added and gently heated without boiling for about 20 minutes, allowed to settle and the clear solution decanted off. Any residue of copper is dissolved in HCl and chlorate of potash and added to the main solution, 1 gram of chlorate is added and the solution boiled to expel free chlorine, 10 cc. more of HCl added, boiled and filtered, the residue being washed with hot water and HCl and the filtrate removed and reserved for determining the sulphur. The residue is washed again with hot water and nitric acid and finally with hot water and ammonia, dried, burnt and weighed. (Where it is posssible to obtain liquid chlorine, its use with HCl in dissolving copper is ideal for this series of analyses.)

148. Sulphur. About 200 miligrams of barium chloride are added to the filtrate from the insoluble residue (the washings with nitric acid and ammonia should be thrown away), and if a notable precipitate of sulphate of barium is

produced, about 300 miligrams more are added, boiled 20 minutes, filtered, the precipitate washed with hot water and HCl, dried, burnt and weighed and the sulphur calculated, remembering that 6 grams of sample were taken for the analysis.

149. Arsenic. The filtrate mentioned in the preceding paragraph is evaporated to a volume of about 100 cc., transferred to a distilling flask of about 250 cc. capacity, 4 grams more of the sample of copper are introduced into the flask, 20 cc. of HCl added, the flask connected with a condenser and the arsenic distilled as described in paragraph 100, omitting to add the ferrous sulphate however, as in this case the metallic copper, 4 grams, is dissolved by the cupric chloride, forming cuprous chloride which reduces the arsenic. The distillation should continue until all of the metallic copper is dissolved and bumping takes place in the flask, when 20 cc. more of HCl should be added and the distillation continued. As the total quantity of sample taken was 10 grams, 1 cc. of the iodine solution is equivalent to about 0.01% As.

150. Antimony. The residue left in the distilling flask is dissolved in a little HCl and hot water, transferred to a large beaker, diluted to about 400 cc. with hot water and is then saturated with sulphurous acid gas, made by boiling sulphuric acid and metallic copper in a separate flask; 11.8 grams of ammonium sulpho-cyanide are now added to precipitate the copper as CuCNS, the mixture is stirred, allowed to settle, filtered and washed with hot water. The filtrate contains very little copper and all of the impurities as, antimony, lead, bismuth, nickel, and cobalt. The excess of sulphurous acid is expelled by boiling and then the heavy metals are precipitated by means of hydrogen sulphide, the contents of the beaker are warmed, filtered and washed with hot water and sulphuretted hydrogen and the filtrate set aside for the determination of the nickel and cobalt (see paragraph 153). The antimony sulphide is dissolved through the filter into a clean beaker by means of a weak solution of caustic potash and determined as described in paragraph 93. In this case the arsenic has been eliminated.

151. Lead. The residue on the filter contains the lead and bismuth. It is dissolved in a few ccs. of nitric acid and hot water, separated from the filter paper, 3 cc. of H_2SO_4 added, evaporated to dense white fumes, cooled, diluted with water, filtered after boiling and the lead determined, as described in paragraph 76.

152. Bismuth. The filtrate from the lead is neutralized with ammonia, an excess of a solution of ammonium carbonate added and the bismuth determined, as described in paragraph 119.

153. Nickel and Cobalt. The filtrate mentioned in paragraph 150 is boiled to expel excess of sulphuretted hydrogen, about 3 cc. of nitric acid added, boiled, neutralized with caustic potash, boiled, allowed to settle, filtered and washed with hot water and the filtrate thrown away or, if desired, it may be tested for zinc. The nickel and cobalt on the filter are dissolved in about 30 cc. of ammonia diluted with hot water, boiled and filtered on the same filter as before, washed with hot water and ammonia, 5 cc. of sulphuric acid and 20 cc. ammonia added to the filtrate, which is diluted to a volume of about 130 cc. and the nickel and cobalt precipitated in metallic form by electrolysis. (See paragraph 120.)

154. Oxygen. While there are direct methods for determining oxygen, it

is generally taken as representing the difference between 100 per cent. and the sum of the content in copper, silver, gold, insoluble residue, iron, sulphur, arsenic, antimony, lead, bismuth, nickel and cobalt, although tellurium and selenium are also sometimes found in bar copper.

REFINED COPPER.

155. The principal impurities in refined copper are arsenic, bismuth, antimony and silver, and as their percentage very small, they are generally determined from 50 grams of the sample. First, 30 grams are dissolved as described in paragraph 147, using five times the quantities of reagents indicated. When dissolved, 20 grams more of the sample are added and 30 cc. of HCl and the distillation of the arsenic effected in a half liter flask. In determining the antimony as described in paragraph 150, it is necessary to add 60 grams of ammonium sulpho-cyanide. In the silver determination, 50 grams of the sample are dissolved in about 400 cc. cold water and 200 cc. nitric acid and finished as described in paragraph 144, but without filtering off gold or residue.

COAL AND COKE.

156. Moisture. One gram of the sample is placed in a weighed platinum crucible and exposed for about 20 minutes to a temperature between 100° and 120° Centigrade. The loss in weight is moisture.

157. Volatile Matter. The top of the platinum crucible, which should fit tightly, is now put on and the crucible placed inside of a 10-gram clay crucible, covered with clean pieces of small coke, a scorifier placed on top of the fire-clay crucible as a cover and the whole placed at the back of a very hot muffle for about 20 minutes. After cooling, the platinum crucible is carefully extracted and weighed, the additional loss of weight representing volatile matter. The object of the above is to prevent the entrance of oxygen and the consequent oxidation of the fixed carbon. Some chemists even place a small amount of a volatile salt, as ammonium carbonate, in the crucible to expel the air. This procedure might be necessary in the case of a coke containing insufficient volatile matter to expel the air, but is not necessary in the case of a coal.

158. Fixed Carbon. The cover is now taken off of the platinum crucible which is then exposed to heat and plenty of air, either in a muffle or over a blast lamp, until the ash appears almost white and all carbon is burnt off. The crucible is then cooled and weighed, this loss in weight representing the fixed carbon. In this weighing, the amount of ash is obtained, which with the moisture, volatile matter and fixed carbon should make a total of 100 per cent.

159. Ash Analysis. About 10 grams of the sample of coal or coke are burnt in a scorifier to ash which should appear as free from carbon as that mentioned above. Half a gram of the ash is then weighed up and treated as described in paragraphs 7 to 25 inclusive, and also 31, for the determination of silica, iron, alumina, lime and magnesia, making the lime determination upon the precipitate of oxalate of lime mentioned in paragraph 24, omitting, however, the treatment with sulphuretted hydrogen, as no heavy metals are liable to exist in the ash.

160. Sulphur. Half a gram of the combustible is treated in a casserole with 2 cc. of water and 5 cc. of nitric acid, the latter being added, little by little, the casserole is covered with a watch glass and after the first violent action has

ceased, 5 cc. more of nitric acid and 1 gram of chlorate of potash are added and sulphur determined by the method already described in paragraphs 78 and 79. The sulphur generally exists as pyrites and is therefore included in the percentages of volatile matter and fixed carbon already found.

WATER ANALYSIS.

161. Total Solids. Half a litre of the water is evaporated to a volume of about 30 cc., transferred to a weighed platinum dish, evaporated almost to dryness at a gentle heat, then to complete dryness on a water bath or in such a manner that the temperature may not rise higher than 140° Cent., during an interval of about 20 minutes after dryness has been obtained. The dish is then cooled and weighed, the increase of weight representing the total solid residue.

162. Volatile and Organic Matter. The dish containing the residue is heated in a muffle or over a blast lamp, cooled and weighed, the loss representing volatile and organic matter.

163. Silica, Iron, Alumina, Lime and Magnesia. These are determined on ½ gram of the residue according to methods described in paragraphs 17 to 25, but in this case it is not necessary to fuse with carbonate of soda nor use hydrofluoric acid nor sulphuretted hydrogen.

164. Sulphates. One hundred cc. of the sample of water is boiled about 20 minutes with 5 cc. of HCl and sufficient barium chloride to effect precipitation of the sulphur as sulphate. The precipitate is then filtered, washed, calcined and weighed as $BaSO_4$, which, multiplied by 0.343, gives the percentage of SO_3.

165. Chlorine. To 100 cc. of the sample is added a little of the chromate of potash indicator, mentioned in paragraph 113 and titrated with the solution of nitrate of silver. In this case, the quantity of the silver nitrate solution consumed in the blank assay, should *not* be deducted. The various results are obtained as so many grams or fractions of gram per liter and after determining the specific gravity with a hydrometer can be transposed into any other manner of reporting.

COPPER REFINERY ELECTROLYTES.

166. Free Acid. A standard solution of ammoniacal copper is prepared by dissolving about 20 grams of copper sulphate in hot water, adding 150 cc. of concentrated ammonia and diluting with cold water to a volume of 1 liter. To standardize this solution, another solution of dilute sulphuric acid is prepared by diluting to 1 liter with cold water, 56.8 cc. of sulphuric acid of specific gravity 1.84; 1 cc. of this solution should contain exactly 0.1 gram of H_2SO_4. (If great delicacy is required, this solution may be standardized by determining its strength gravimetrically as in paragraph 164.) Ten cc. of the dilute sulphuric acid is taken by means of a pipette and titrated with the ammoniacal copper solution, the end point is reached when a very faint but persistent milky precipitate is obtained.

167. In the analysis 10 cc. of the sample of electrolyte are titrated with the ammoniacal copper solution and the number of grams of free acid per liter is calculated. To obtain percentage, divide the number of grams per liter by 10 and then by the specific gravity of the electrolyte as indicated by the hydrometer.

168. Copper. Ten cc. of sample are taken, 3 cc. nitric acid added and boiled to peroxidize the iron, 10 cc. of ammonia added and after cooling, titrated with potassium cyanide.

169. Chlorine. Five cc. of the sample is boiled with 10 cc. of the solution of caustic potash mentioned in paragraph 113, carefully neutralized with the solution of nitric acid and the determination finished as described in paragraph 116. The percentage is calculated, taking into consideration the specific gravity of the electrolyte.

170. Iron. Ten cc. are peroxidized with 3 cc. of nitric acid, then precipitated with ammonia and the iron determined as described in paragraph 146, latter part.

171. Arsenic. Ten cc. are placed in a small distilling flask of about 1 ounce capacity, 5 cc. HCl and 1 gram of *ferrous*-sulphate added and the arsenic determined by distillation as described in paragraph 100.

172. Antimony, Bismuth, Nickel and Cobalt. The four elements are determined in the residue remaining in the distilling flask mentioned in the preceding paragraph, according to the methods described in paragraphs 150 to 153, but instead of adding 11.83 grams of ammonium sulpho-cyanide, as mentioned in paragraph 150, only sufficient should be added to precipitate the copper present.

REFINED LEAD AND LEAD BULLION.

173. The sample is cut into thin strips, cleansed with dilute HCl, dried, exactly 108.4 grams weighed and dissolved in 600 cc. of hot water and 130 cc. of nitric acid. Should there remain a white residue, it is probably silver chloride, but may also be Sb_2O_5; it is filtered off, washed with dilute nitric acid and reserved; 35 cc. of sulphuric acid, previously diluted in cold water, are now added to the filtrate and the whole transferred to a liter flask and mixed, diluted to 1 liter with cold water, mixed, allowed to settle and exactly 900 cc. of the supernatant liquid (corresponding to 100 grams of the sample) are drawn off, the precipitate of Sb_2O_5 added, and the whole evaporated to dense white fumes, allowed to cool, 50 cc. cold water added, boiled, filtered and the filter washed with hot water and dilute sulphuric acid. The precipitate is thrown away. To the filtrate is added sulphuretted hydrogen, gently warmed, filtered and washed with hot water and H_2S water. The filter holds silver, copper, arsenic, antimony, bismuth and possibly cadmium. The filtrate holds the iron, zinc, nickel and cobalt.

174. Arsenic and Antimony. The precipitate on the filter is treated with dilute caustic potash to dissolve arsenic and antimony and their determination finished as per paragraph 93, commencing with the thirteenth line.

175. Bismuth. The precipitate from the preceding paragraph, which has been freed from arsenic and antimony, is dissolved in nitric acid as in paragraph 119, bismuth precipitated and weighed as Bi_2O_3.

176. Copper. This is precipitated in the filtrate from the bismuth, with H_2S, filtered, redissolved in nitric acid and determined by electrolysis or by the iodide method.

177. IRON. The filtrate mentioned in the last line of paragraph 173 is made ammoniacal, the sulphides allowed to settle, filtered and washed with hot water containing H_2S. The filtrate is thrown away. The precipitate is treated with very dilute hydrochloric acid to dissolve iron and zinc only, leaving the

nickel and cobalt on the filter. The iron in solution is peroxidized with 3 cc. nitric acid, precipitated with ammonia, boiled, filtered, washed with hot water containing ammonia, dried, burnt and weighed as Fe_2O_3; this weight, multiplied by 0.7 (exactly 0.6994) gives Fe.

178. Zinc. The filtrate from the iron is neutralized with acetic acid, made slightly alkaline with ammonia, the zinc precipitated with H_2S, filtered, washed with hot water, dissolved in a minimum quantity of dilute HCl, boiled, precipitated with sodium carbonate, boiled, filtered, washed, ignited and weighed as ZnO. (After washing and before igniting, it is well to moisten the precipitate with a small amount of ammonium nitrate.) ZnO multiplied by 0.8 gives Zn.

179. Nickel and Cobalt. The precipitate of the sulphides of nickel and cobalt, mentioned as being left on the filter in paragraph 177, is dissolved in dilute nitric acid, reprecipitated with sodium carbonate, filtered, washed, ignited and weighed as Ni_3O_4, plus Co_3O_4, which multiplied by 0.73, gives Ni plus Co.

In the case of lead bullion containing appreciable quantities of impurities, it is advisable to take an initial weight of less than 100 grams of the sample, say 10.84 grams.

180. Silver and Gold. These are determined by simply cupelling a number of charges of 10 grams or ½ A. T. each, and after weighing the resultant silver beads, combining a number of them, to be parted for gold.

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