| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | 0.0244 | 0.0740[1] | 0.0268 | 0.0555[1] | 0.0159 | 0.0298 | 0.0174 | 0.0113 | 0.0263 Gm. |

The following determinations were made of fluorine in natural rocks and compared with the gravimetric results:

| | | | |
|---|---|---|---|
| Gravimetric determination | 0.15 | 3.01 | 3.01 per cent. |
| Colorimetric determination | 0.21 | 2.58 | 3.20 per cent. |

A number of determinations of fluorine were made in rocks containing quantities varying from 10 to 20 per cent., but the results were not satisfactory, being several per cent. out of the way.

CHEMICAL LABORATORY.
U. S. GEOLOGICAL SURVEY,
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## VOLUMETRIC METHOD FOR THE DETERMINATION OF ZINC.

BY WM. HERBERT KEEN.

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Several schemes have been advanced for the estimation of zinc by titration with potassium ferrocyanide, but so far no one of them has found universal application. The methods which have found favor are either so complicated or so difficult in manipulation that a large personal error is always introduced and it seldom happens that very close checks are obtained by different operators, even when the same procedure is followed. Nearly a year ago I became interested in the volumetric determination of this metal with the idea of substituting it for the rather tedious gravimetric method which has always been in use in our laboratory.

At first, and for quite a long time in fact, I was not very successful and encountered numerous difficulties. The samples which I used in this preliminary work were spelters, the zinc content of which had been very carefully determined by difference. Finally, after a trial of all the methods which seemed reliable, with varying successes, I concluded that changes might be made to good advantage in nearly all of them, so with what experience I had already gained, I attempted to work up a scheme which would embody the good points of all of these methods and as far as possible none of the bad ones. The method which I am about to describe, therefore, is not new, but is rather a re-modeling of the older ones. The scheme is one which is identical in certain parts for almost every condition, but there are some slight variations which are necessary for different products and, if accuracy is desired, they should be observed. Accordingly, I will describe the method, applying it to typical cases.

*Preparation of the Ferrocyanide Solution.*—Dissolve crystals of c. p. potassium ferrocyanide in water in the proportion of 22 grams to the liter. If the solution is not clear, it should be filtered before it is diluted to the desired volume. It is a good plan to make up several liters at a

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[1] In these two cases the silica was filtered immediately after being precipitated with ammonium carbonate, which accounts for the large quantity found.

time, as the solution remains constant almost indefinitely, and if many determinations are necessary, a bottle of fifteen, or even twenty, liters of solution will not last very long.

*Preparation of the Standard Zinc Solution.*—This solution should be made up with the greatest care, as all subsequent work depends on its accuracy. In order to make up two liters, weigh very carefully and transfer to an 800 cc. beaker 10 grams of c. p. zinc or an equivalent weight of the oxide (12.4465 grams)—if the latter is used, it must be freshly ignited, cooled in a desiccator—and dissolved in 50 cc. of hydrochloric acid diluted with water. Heat until solution is complete and then dilute to about 300 cc. and add a considerable excess of bromine water. Heat until the bromine is entirely expelled. Wash the cover glass and the sides of the beaker and add an excess of ammonia. Put in a warm place on the hot plate where it will remain just below the boiling-point, or boil very gently for about fifteen minutes. By this time the small amount of iron, which is nearly always present, should be completely precipitated. Filter carefully into a graduated liter flask, washing the beaker and precipitate once with water containing a little ammonia and then several times with hot water. Replace the flask under the funnel by a small beaker (about 250 cc. capacity) and dissolve the iron precipitate in hot dilute hydrochloric acid. Re-precipitate the iron with ammonia and filter again, adding the filtrate to the main solution. Burn the filter paper containing the iron precipitate and ignite. Weigh as $Fe_2O_3$ and calculate to Fe, deducting this weight from the original 10 grams of zinc. Sometimes small amounts of silica and dirt are also present in the so-called c. p. zinc, and the weight of this should also be deducted. These are small corrections and make very little difference as a rule, but it is always well to make them, as it gives the operator more confidence in his results and leaves no loop-hole for inaccuracy in later work. Now make the solution barely acid, using a small piece of litmus paper as an indicator and add 30 cc. of hydrochloric acid in excess for each liter of solution. Add also 10 grams of ammonium chloride for each liter. Dilute to the mark with water, after cooling, and pour carefully into a *dry* two-liter bottle. Do not wash out the flask, but after it has drained as much as it will, fill it to the mark with distilled water and add this to the rest of the solution. Shake until thoroughly mixed and the solution is ready for use. Its value will be 0.0050 gram of zinc per cc. of solution—less a small correction due to the impurities deducted from the original weight.

*Standardization.*—By means of standard pipettes, measure out three portions of the zinc solution of 20 cc. each, three portions of 50 cc., three of 70 cc., and three of 100 cc., into 400 cc. beakers of the wide shallow type, which will greatly lessen the amount of stirring necessary in order to obtain a homogeneous solution after each addition of the ferrocyanide. Add about 1 cc. of hydrochloric acid to each of the smaller portions. Dilute each to 150 cc. and all are ready for the titration. Except for very accurate work it is not necessary to take more than three or four portions altogether (one for each amount) to determine the average value of the ferrocyanide solution, but it has been found[1] that a slightly different factor should be used for different amounts of zinc, hence the necessity in accurate work for establishing these factors for amounts of solution likely to be used most frequently. Fill a clean burette with ferrocyanide, heat one of the portions of zinc chloride nearly to boiling and titrate as follows: Pour off about 20 cc. of the hot zinc solution into a small beaker and set it aside. Titrate the remainder by running in ferrocyanide, a few cc. at a time, until a drop tested on a porcelain tile with a drop of a five per cent. solution of uranium acetate shows a decidedly brown color. Now add all but about 2 cc. of the reserved portion, and having tested to be sure that the endpoint is not now overstepped, add the ferrocyanide in portions of half a cc. at a time until the end point is again passed. Finally add the last of the reserved portion, washing it all out with distilled water and carefully washing down the sides of the titration beaker, and finish the titration by adding two drops at a time, testing after each addition. The endpoint at this time will be sharper if instead of one drop two or three drops are added to the drop of uranium acetate on the tile. The amount of zinc lost at this stage of the titration will be so small as to be insignificant. When the final distinctly brown tinge is obtained, wait a minute and observe if one or more of the preceding tests do not also develop a color. Note the number of spots by which the endpoint has been overstepped, and since each test means an addition of two drops, or 0.1 cc. of solution, make the necessary correction when reading the burette. A blank should also be made and the final reading and all other readings corrected by this amount. The blank should be made with a solution containing 10 cc. of hydrochloric acid, neutralized with ammonia, made acid again, and after 3 cc. of acid have been added in excess, diluted to 150 cc. and heated nearly to boiling. This will usually require about 0.2 cc. to give a decided test. Run all the titrations in the same way and calculate the values for one cc. of the solution for the different portions, taking the average of the three results in each case if they are close enough (it is easy to obtain checks within 0.1 cc.), thus obtaining the different factors for the varying amounts of zinc—or what is equivalent to the same thing, for varying amounts of ferrocyanide. In actual work later, the factor should be used for the amount of solution which corresponds most nearly to that required for the titration. Ordinarily, however, the one average

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[1] This Journal, 29, 205.

factor for three or four different amounts of zinc will be accurate enough for all determinations.

The last solution which I standardized had the following factors:

| Standard zinc solution. | Grams of zinc. | Ferrocyanide solution. | Factors. |
|---|---|---|---|
| 20 | 0.09995 | 19.4 | 0.005152 |
| 50 | 0.24988 | 48.1 | 0.005195 |
| 70 | 0.34983 | 67.2 | 0.005206 |
| 100 | 0.49975 | 95.5 | 0.005233 |

Greater accuracy could be obtained with a slightly weaker solution, say, 15 or 18 grams to the liter, but for general application I find a solution of the above strength the most convenient.

*Determination of Zinc in a Spelter.—Method of sampling.*—There are several methods in common use, but probably the most accurate one is to break off small pieces from slabs in different parts of the pile until enough has been obtained to make a fair average—say five pounds for each car load, if the shipment is homogeneous. The sample thus obtained should then be heated in an ordinary clay crucible until just melted, when it should be poured into a wooden box, previously rubbed with chalk—and shaken violently. A box suitable for this must be made with tight joints and no cracks and should be supplied with a cover. This treatment should result in a finely granulated sample. Screen out the coarser pieces by passing through a 20-mesh and reduce the bulk of the fine stuff by coning and quartering until a small working sample is obtained. This not only will be found very easy to weigh, but will in addition almost perfectly represent the whole consignment.

*Analysis.*—Weigh five grams of the sample of spelter, place in a 600 cc. beaker, cover with a watch-glass and dissolve in 50 cc. of hydrochloric acid (1.20) diluted with water. Heat until completely dissolved. The evolution of hydrogen, occasioned by the solution of the zinc, precipitates such metals as copper, lead and tin; but the heating should be continued until these metals go into solution again, as they occlude small amounts of zinc. When solution is complete, neutralize with ammonia and reacidify with hydrochloric acid (1.20), adding 5 cc. in excess, dilute to about 300 cc. and pass a current of hydrogen sulphide gas through the warm solution for about twenty minutes. If the precipitated sulphides do not settle readily, allow the solution to stand for an hour or so at a temperature just below the boiling-point. This will not be necessary, unless tin is present. Filter off the sulphides, allowing the filtrate to run into an 800 cc. beaker and wash the filter thoroughly with hot water. Heat the filtrate to gentle boiling and after the free hydrogen sulphide has been expelled add a large excess of bromine water and continue the boiling until the bromine has been expelled. Now add a large excess of ammonia and boil gently for about fifteen minutes. If the amount of iron is considerable, it will not be necessary to boil so long, as it is only in the case of very small amounts that the precipitation is likely to be incomplete, unless the boiling is continued. Filter into a graduated liter flask, washing first with dilute ammonia—both the beaker and the filter—and then with hot water. Put about 10 cc. of hydrochloric acid (1.20) in the beaker, dilute with hot water and pour it over the precipitate on the paper, allowing it to run through into a small beaker of about 250 cc. capacity. Re-precipitate with ammonia and filter into the main solution in the flask, washing as before. If the amount of iron is very large, a third precipitation will be necessary, but in the ordinary spelter this is not the case. Put a small piece of litmus paper in the flask and add hydrochloric acid (1.20) until the solution is just acid, and then add 30 cc. in excess. Cool to room temperature and then make up to the mark with water. After mixing the solution thoroughly by several decantations back and forth from the flask to a beaker, measure out several portions of 100 cc. each (equivalent to 1/2 gram of spelter) by means of a pipette. I find it convenient to use a 400 cc. beaker for the titration. Usually only one portion is necessary, but it is well to have a second one in reserve. Dilute to 150 cc., heat nearly to boiling (about 85°) and titrate with ferrocyanide, as described in the procedure for standardization. Calculate the percentage of zinc by multiplying the standard value of one cc. by the number of cubic centimeters required (less the blank) and divide by 0.5, the weight of spelter taken as a sample.

*If manganese is present* in the spelter—a rare occurrence—the above result will be too high. If time is an object, the quickest way to overcome this difficulty is to make a separate determination of the manganese, although it may be removed before titration in a way I shall describe later. To determine the manganese, the best and most rapid way is to use the Bismuthate Method as applied to steels. Dissolve 1 gram of the spelter in a 150 cc. Erlenmeyer flask in 50 cc. of nitric acid (1 to 3) and boil off the nitrous fumes. Cool in ice-water and add about a gram of sodium bismuthate. If manganese is present, the pink color of permanganic acid will develop at once. If such is the case, filter through an asbestos filter into a 300 cc. Erlenmeyer, washing with 100 cc. of ice-cold 3 per cent. nitric acid. Add a measured amount of ferrous sulphate solution (12 grams to the liter) until the solution is perfectly colorless; titrate the excess with a standard permanganate solution (1 gram to the liter). Subtract the volume of permanganate required from the amount of the latter equivalent to the volume of ferrous sulphate used and multiply by the manganese value of the permanganate solution. The factor is about 0.00035 for a solution of this strength. This will give the percentage of manganese in the spelter. The chemical equivalent of this amount in zinc should be deducted from the percentage of zinc previously obtained.

*If cadmium is present,* it will also remain in solution with the zinc and will affect the titration in a manner similar to the manganese. It is usually present in such very small amounts that it is not readily precipitated by hyrdogen sulphide except from a nearly neutral solution, in which part of the zinc is also precipitated. It is therefore necessary to make a separate determination of the cadmium and correct the apparent amount of zinc, as was done in the case of manganese. Another alternative, which has given me doubtful success in the case of such small amounts, is to boil the solution for a few minutes with a piece of aluminum foil just previous to titration. The aluminum thus introduced into the solution does not affect the result. Usually, however, unless specially asked for, cadmium is always counted as zinc.

*To Determine Zinc in Ores.*—Decompose one gram of the sample in a beaker with hydrochloric acid, or if necessary with aqua regia. Evaporate to dryness, and if nitric acid has been added, re-dissolve in hydrochloric acid and evaporate again. Dissolve in 15 cc. of hydrochloric acid (1.20), dilute with water, filter and wash. Burn off the filter (unless it contains lead) in a platinum crucible and treat with hydrofluoric and sulphuric acids—exactly as in a silica determination. Dissolve the residue in hydrochloric acid and add to the solution. Usually this treatment of the residue is not necessary, as it rarely contains more than a few hundredths of a per cent. of zinc. If lead sulphate is present in this residue, use a perforated crucible with an asbestos felt for a filter. Remove the filtrate after washing the residue thoroughly and dissolve out the lead sulphate with a strongly ammoniacal solution of ammonium citrate. Wash with hot water and then transfer the remaining residue, together with the felt, to an ordinary platinum crucible and treat wih hydrofluoric acid as before, finally adding the hydrochloric acid solution of the remaining residue to the filtrate. (Advantage may be taken of the above steps to determine the lead in the same portion—the only changes necessary being to evaporate with sulphuric acid instead of hydrochloric and to weigh the perforated crucible before and after treatment with the ammonium citrate, calling the difference lead sulphate.) Neutralize the filtrate with ammonia and again acidify, adding about 3 cc. of acid in excess for every 200 cc. of solution. Pass hydrogen sulphide through the solution to remove the copper group and, having filtered out the precipitate thus obtained, heat until the free hydrogen sulphide has boiled off and then add an excess of bromine water and evaporate to about 50 cc. Precipitate the iron with ammonia, using a large excess and washing with water containing ammonia. If the precipitate amounts to more than a few tenths of a per cent. it should be dissolved and reprecipitated and in case of large amounts of iron a third precipitation is sometimes necessary. Acidify the filtrate with hydrochloric acid, adding 3 cc. in excess. The solution is now ready for titration, unless manganese is present, if its volume does not exceed 150 to 200 cc. If it is of larger bulk than this, it should be evaporated until of approximately this volume, before titration. In the case of very large amounts of iron the sulphide of zinc should be separated from it just as described below when nickel is present, or, if preferred, the ether separation may be used.

*When Manganese is Present in the Ore.*—If the iron is small in amount, add to the solution after evaporation, but before removing the iron, five grams or more of potassium or sodium bromide. Make strongly ammoniacal and stir for an hour by means of some such device as that used for the solution of steels in the determination of carbon. If no appliance of this sort can be had, the solution should be allowed to stand over night at room temperature. The manganese and iron are completely precipitated and should be filtered off and washed with water containing ammonia. The filtrate should then be acidified as above and titrated. If the iron is present in large enough quantities to require re-precipitation, it should be removed before treatment with the bromide; but if both the manganese and iron are precipitated together, as above, and it is desired to re-precipitate them, they should be dissolved in a mixture of hydrochloric and sulphurous acids, the solution boiled to expel the sulphurous fumes and then oxidized with bromine water. The bromine should be boiled off as before and the precipitation then repeated with the alkali bromide and ammonia. The amount of bromide may be varied without any effect on the titration. If it is desired to determine the manganese, it may be dissolved in sulphurous acid alone, and after solution is complete, nitric acid added, the nitrous fumes boiled out and the determination completed by the Bismuthate Method.

Of course the manganese may be readily avoided by precipitating the zinc as sulphide from a slightly acid solution and this is to be advised in the case of large amounts of manganese—also, if any nickel is in evidence. The presence of nickel will be made known by a blue color of the ammoniacal filtrate from the iron. If it is necessary to precipitate the sulphide of zinc to avoid these metals, the best plan is to evaporate the hydrochloric acid as first obtained to a small bulk in order to expel most of the free acid, dilute with a little water and neutralize with sodium carbonate solution, using methyl orange as an indicator. The neutral point should be carefully obtained and then *ten drops* of hydrochloric acid added. Wash down the sides of the beaker, dilute to 200 cc. and pass hydrogen sulphide through the *cold* solution for an hour. Let the solution stand for several hours, or, if convenient, over night before filtering. Zinc sulphide precipitated in this way should filter out like so much sand. Put the paper containing the precipitate into a beaker and digest until dissolved in 10 cc. of hydrochloric acid diluted with water. Pass hydrogen sulphide for a few minutes to be sure that all the copper is precipitated and then filter and wash thoroughly with hot water. Evaporate the filtrate after adding a slight excess of bromine water to oxidize any iron that may have been occluded by the zinc, and when it is reduced to a small volume add an excess of ammonia and boil. Filter, if necessary, and neutralize the filtrate with hydrochloric acid, adding 3 cc. in excess. Dilute to 150 cc. and titrate. This method is excellent if the conditions are just right, but my idea has been to avoid a precipitation of the zinc, if possible, and thus get rid of what may be a troublesome filtration. Accordingly, I have endeavored, except in cases where nickel is present, to precipitate from the zinc all metals interfering with the titration.

*Brasses.*—Remove the tin, copper and lead in the usual way—by solution in nitric acid, filtration of the metastannic acid, and deposition of the two latter metals by electrolysis. If it is certain that the copper is entirely removed, evaporate to dryness the nitric acid solution, which now contains only the zinc and perhaps a small amount of iron. Dissolve the residue in 10 cc. of strong hydrochloric acid and, after dilution, precipitate the iron with ammonia, being careful to boil long enough to insure a complete precipitation, as iron comes down very slowly when present in such small quantities. Filter and wash with dilute ammonia water and then with hot water. Neutralize the filtrate with hydrochloric acid, add an excess of 3 cc., dilute to 150 cc., and titrate with the standard ferrocyanide solution. In the case of a manganese bronze, the only modification would be the treatment with alkali bromide, as described above under ores.

It is sometimes easier, in the case of brasses, to make the filtrate from the electrolysis ammoniacal and add colorless ammonium sulphide. Digest at a temperature near the boiling-point for about an hour, allow to settle and filter, keeping as much of the precipitate in the beaker as possible. When the liquid has run through the funnel, replace the filtrate beaker by the one containing the precipitate and pour dilute hydrochloric acid over the filter, allowing it to run through on to the main bulk of the precipitate. Wash the filter once or twice and heat the solution until the zinc is dissolved. Pass a current of hydrogen sulphide for a few minutes and filter out any small traces of copper that may be precipitated as sulphide. Oxidize the filtrate with bromine water and evaporate to a small volume, finally precipitating the small amount of iron and finishing as before.

*Aluminum Alloys Containing Zinc.*—Aluminum does not affect the ferrocyanide and so the natural idea would be to dissolve in hydrochloric acid and proceed directly with the titration as soon as solution was complete. But iron is almost always present in such alloys to a considerable amount, and hence the necessity for a more roundabout method. Dissolve one gram in either nitric or hydrochloric acid. Add a few crystals of citric acid, make ammoniacal, and heat to boiling. Remove from the source of heat and add a little colorless ammonium sulphide. Allow to settle and then filter, being careful to wash out the last traces of citric acid with a wash water containing a little ammonium sulphide. The precipitate will consist of sulphide of zinc, iron and copper metals. Treat it exactly as described for brasses under similar conditions. If desired, the metal may be dissolved in hydrochloric acid and the zinc precipitated as sulphide from a slightly acid solution just as when it is required to separate it from nickel.

In general, any one working intelligently, realizing the final conditions and knowing something of the material in hand, will find no difficulty in following out the plan of this method.

LABORATORY OF BOOTH, GARRETT & BLAIR,
Philadelphia.

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# THE DETERMINATION OF BENZENE IN ILLUMINATING GAS.

BY L. M. DENNIS AND ELLEN S. MCCARTHY.

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## I. The Absorption of Benzene by Ammoniacal Nickel Nitrate.

In 1903 Dennis and O'Neill described[1] an absorption method for the determination of benzene in illuminating gas. The absorbent there recommended was an ammoniacal solution of nickel nitrate, the use of such a solution for the determination of benzene having been suggested by the statement of Hofmann and Küspert[2] that when illuminating gas acts upon a mixture of nickel hydroxide and ammonia, there is formed a compound of nickel cyanide with ammonia and benzene, $Ni(CN)_2.NH_3.C_6H_6$.

In practice, this method for the determination of benzene in some localities, has given most excellent results, while in other quarters it has been far from satisfactory. Morton recently demonstrated[3] that when mixtures of *benzene and air* are analyzed with the use of the reagent, the results are scarcely better than might be obtained with water alone, and that, moreover, the efficiency of the absorbent steadily decreases as the amount of benzene that it has taken up increases. These statements of Morton have been substantiated in this laboratory and the

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[1] This Journal, 25, 503.

[2] Z. anorg. Chem., 15, 204 (1897.)

[3] This Journal, 28, 1728 (1906).