ON THE VOLUMETRIC DETERMINATION OF TITANIC ACID AND IRON IN ORES.

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THE difficulties connected with the gravimetric determination of titanic acid make a reliable volumetric method very desirable, especially for the analysis of titanic iron ores. We have therefore turned our attention to this subject and have found that satisfactory results can be obtained by a slight modification of a process which has long been known.

About thirty years ago, F. Pisani[1] stated that the acid under consideration could be determined by reduction with zinc in hydrochloric acid solution, using a gentle heat, and when the violet color no longer deepened, pouring off the liquid from the remaining zinc and titrating with potassium permanganate. Pisani gave no test analyses, and, since his process has not been generally adopted, it is evident that it has not proved satisfactory in the hands of others.

A number of years ago one of us (Wells) had occasion to analyze a large number of titanic iron ores and attempted to use Pisani's method with the use of sulphuric acid instead of hydrochloric acid, as recommended by the originator of the process. This modification was made on account of the well-known interference of chlorides with the permanganate method, and it was found that the difficulty mentioned by Pisani, that titanic acid was liable to be precipitated by heating sulphate solutions, could be readily overcome by using a sufficiently large quantity of sulphuric acid. The results of a great many trials at that time, however, showed that the method gave very low results, and the process was then abandoned. The process used in the experiments just referred to was precisely the same as that which we now recommend and which will be described in detail below, except that after reduction with zinc the solution was poured off, from the excess of that metal, into a beaker for titration, an operation which Pisani recommended, and which is customary in the determination of iron by this method. It is now evident that the failure of the method was due to the contact of

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[1] *Compt. rend.*, 59, 289.

the solutions with atmospheric air, for, while ferrous sulphate is acted upon very slowly, the sulphate corresponding to the lower oxide of titanium is very rapidly oxidized under such circumstances.

Marignac,[1] with his accustomed skill, applied Pisani's method, soon after its publication, to the determination of titanic acid in the presence of niobic acid. He was obliged to use special conditions in order to avoid the reduction of the other acid at the same time, but the feature of his process which is interesting in the present connection is that he reduced the titanic acid by means of a long rod of pure zinc extending up into the neck of the flask which held the solution, and, after allowing the reduction to take place out of contact with air, he finally took out the zinc and titrated directly in the flask without transferring. Marignac gave a number of test analyses which showed that the method gave very good results, although they were a little too low with the larger quantities of titanic acid used.

We have modified the method of Pisani as improved by Marignac by using sulphuric acid solutions and by protecting the liquid during cooling and titration by means of carbon dioxide, and we have also arranged the process for the determination of iron along with the titanic acid. The details of the operation are as follows:

Five grams of very finely pulverized ore are placed in a rather large beaker covered with a watch-glass and treated with about 100 cc. of concentrated hydrochloric acid. A very gentle, gradually increasing heat is applied for several hours, more hydrochloric acid is added if necessary, and when no further action is apparent about fifty cc. of a mixture of equal volumes of concentrated sulphuric acid and water are added and the whole is evaporated until the sulphuric acid fumes strongly. After cooling, about 200 cc. of water are added, the whole is heated until the sulphates are dissolved, and the liquid is filtered into a liter flask. With many titanic ores this operation will have dissolved everything except silicious matter. If, however, some undissolved ore remains, it is ignited, to burn the filter-paper, in a platinum crucible, and the residue is fused with potassium

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[1] *Ztschr. anal. Chem.*, 7, 112.

disulphate, at a gradually increasing heat, up to low redness, until the black particles have disappeared. To the cake in the crucible several volumes of concentrated sulphuric acid are added, heat is gradually applied until the whole becomes liquid, then this is heated with a moderate volume of water to dissolve the sulphates, and the liquid is added to the main solution in the liter flask. Filtration may be omitted here, or in the case of the original solution, provided that the silicious matter is not to be weighed.

The liquid in the liter flask is diluted to the mark and mixed, and four portions of 200 cc. each, representing one gram of ore, are taken, two of them into Erlenmeyer (conical) flasks of 500 cc. capacity, and the other two into ordinary flasks of 350 cc. capacity.

To determine iron, hydrogen sulphide is passed into the solutions in the ordinary flasks until they are saturated with the gas, then inverted porcelain crucible covers are placed upon the mouths of the flasks and the solutions are heated and boiled continuously, so that air cannot enter, until the hydrogen sulphide has been completely removed. This point can be determined by testing the escaping steam with paper which has been dipped in a solution of lead acetate made strongly alkaline with potassium hydroxide. The flasks are then quickly filled to the neck with cold distilled water which has been recently boiled, best by means of an inverted wash-bottle, directing the stream against the neck of the flask in such a way that the water does not mix to a great extent with the heavier sulphuric acid solution. If the stream of cold water does not strike the top of the neck, there is little danger of breaking the hot glass. The contents of the flasks are now rapidly cooled by means of a stream of water, transferred to large beakers, and titrated with potassium permanganate solution.

To the solutions in the Erlenmeyer flasks about twenty-five cc. of concentrated sulphuric acid are added, then in each case three or four rods of chemically pure zinc, about fifty mm. long and six or seven mm. in diameter, are attached to the loop of a porcelain crucible cover, which is larger than the mouth of the flask, by means of platinum wire wound securely around them near the middle. The length of the wire is so arranged that the pieces of zinc will be suspended in the liquid when the cover is placed on the flask. When this has been accomplished the liquid is boiled gently, so as to keep out air, for thirty or forty minutes. then, without interrupting the boiling, a glass tube, so bent that it extends fifty mm. or more into the flask, which is delivering a rather rapid stream of carbon dioxide, is introduced under the cover. Care should be taken to have the carbon dioxide free from air, and that hydrochloric acid which contains sulphur dioxide is not used for its generation. The flask is now rapidly cooled, and then the zinc is washed with a jet of water and removed, and the solution is titrated with permanganate in the flask while the carbon dioxide is still being passed in. The difference between the permanganate used in this case and that used for the iron alone, represents the amount corresponding to the titanic acid. The factor for metallic iron divided by 0.7 gives the factor for titanic acid (TiO_2).

When a fifty cc. burette is used, the most convenient strength for the permanganate solution is when one cc. is equal to about 0.014 grams of metallic iron, corresponding to seven and nine-tenths grams of potassium permanganate per liter.

It is customary in this laboratory to standardize permanganate solutions by a method which very closely approaches the one described above for the actual determination of iron, so that, if any slight errors are inherent in the process, they are likely to be eliminated because they have an equal effect upon the standardization and the determination. The method is simple and convenient, and a large amount of experience has shown it to be very accurate. To carry out this operation, a 350 cc. flask is half filled with sulphuric acid, (the strong acid diluted with about eight volumes of water). This is heated to boiling with an inverted crucible cover upon the mouth of the flask, and after the air has been expelled, about six-tenths gram of the purest iron wire, representing nearly the average amount of iron in one gram of an ore, is dropped in and gentle boiling is continued until it has dissolved. The flask is filled to the neck with water, cooled and finally the liquid is transferred to a beaker and titrated.

The method of determining iron by reduction with hydrogen sulphide, although well known, does not appear to be as generally used as it deserves to be. The precipitated sulphur present in the liquid has absolutely no effect upon cold permanganate solution, but precipitated sulphides, such as copper sulphide, should be filtered off before boiling. Since concentrated sulphuric acid is an oxidizing agent, care must be taken to use sufficiently dilute solution, and not boil them down until the acid becomes strong.

We have made some test analyses upon the method of determining titanic acid volumetrically. Crude potassium titanofluoride, K_2TiF_6, was recrystallized twice from water and used as the source of titanium. Weighed quantities of the carefully dried salt were evaporated with sulphuric acid, and the resulting substance was treated essentially as has been described above, but with some variations in the time of boiling, the strength of the acid and the amount of zinc used. The following table gives the results obtained in grams :

Potassium titanofluoride taken.	Titanium found.	Titanium calculated.	Error.
0.7638	0.1437	0.1527	—0.0090
0.6425	0.1225	0.1285	—0.0060
0.7778	0.1524	0.1555	—0.0031
0.6793	0.1308	0.1358	—0.0050
0.8226	0.1607	0.1645	—0.0038
1.0956	0.2107	0.2191	—0.0084
0.4451	0.0848	0.0890	—0.0042
0.6359	0.1215	0.1271	—0.0056
0.9004	0.1715	0.1800	—0.0085
0.4634	0.0882	0.0926	—0.0044

The results show a fair degree of uniformity, but they are invariably too low. A part of the deficiency was probably due to the impurities in the potassium titanofluoride used, for it is quite possible that certain impurities may have been increased rather than diminished by recrystallizing it, and it is exceedingly difficult to obtain any titanium compound that is certainly free from all other acid-forming elements. The greater portion of the error was doubtless due to the action of air which gained access to the liquid in spite of the precautions used, and it is evident that the accuracy of determinations made by this method would be increased by adding one-twentieth or one-thirtieth to the amount of titanic acid found under the conditions that we have used.

The great influence of the action of air is shown by two determinations which were made exactly like those given in the above table, except that, after cooling in carbon dioxide, the solutions were transferred to beakers and titrated as quickly as possible.

Potassium titanofluoride taken	Titanium Found.	Titanium calculated.	Error.
0.6831	0.1078	0.1366	0.0288
0.9545	0.1535	0.1909	0.0374

The volumetric method, even without correction, will be likely to give more reliable results than those obtained by gravimetric. determination, unless great care and skill are displayed in carrying out the latter.

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ARSENIC IN GLYCEROL.

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IN following up the literature of glycerol I find that the first to note the presence of arsenic in the medicinal article was Jahns,[2] but he apparently did not investigate the subject thoroughly.

E. Ritsert[3] was the next to take the subject up. He showed the presence of arsenic in seven samples of medicinal glycerol, by the following test, which he says shows 0.001 mg. in one cc. while the Marsh test shows only 0.01 mg. in one cc. One cc. of glycerol is placed in a small measuring cylinder and to this one cc. of water is added, together with fifteen drops of hydrochloric acid and 0.6 gram zinc. The top of the cylinder is covered with filter-paper, moistened with a 1 : 1 silver nitrate solution or saturated mercuric chloride solution, and a yellow stain is obtained on the paper if arsenic is present. Ritsert also states that ammoniacal silver nitrate solution is a good reagent for arsenious acid and that the arsenious acid present probably

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[1] Read at the Springfield Meeting.

[2] Pharm. Ztg., *1888*, 652.

[3] Pharm. Ztg., *1888*, 715, and *1889*, 104, 360 and 625.