as ferrous sulfate or other reducing agents as indicated by Wells,[1] to produce a precipitate. On the other hand, the gold present in the manganese deposits adjacent to other gold deposits may be due wholely to the fact that gold solutions in contact with manganese dioxide yield metallic gold, by virtue of the principle of auto-reduction shown by other peroxides with gold solutions.

The auto-reduction of gold solutions to metallic gold has apparently, thus far, not been considered as an important geological factor in the secondary deposition of gold, but it is doubtless possible that in many instances one can conceive of the oxygen of the air as being the real agent which causes the gold to be reduced in presence of a manganese or similar compound which acts as a catalytic agent.

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THE VOLUMETRIC DETERMINATION OF TITANIUM AND CHROMIUM BY MEANS OF A MODIFIED REDUCTOR.

By C. Van Brunt.

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Shimer and Shimer[2] have described a modification of the method of Newton[3] for the determination of titanium, in which the reduction by boiling with zinc in a flask is supplanted by the use of a Jones reductor. The authors found that the ordinary form of this familiar apparatus, as used in the determination of iron, does not give complete reduction—a fact which the present writer can corroborate. They accordingly substituted a much longer and narrower tube, which modification had the desired effect.

The proposed method seemed to offer a way of escape from the tedious methods in vogue. These must include the original Newton method which, though for most purposes preferable to the gravimetric, is still lacking, mainly because of the slow disappearance of the last portions of the zinc, and the difficulty of preventing, with certainty, during this stage, the partial reoxidation of the very sensitive hot titanous solution.

But in practice in this laboratory, the Shimer reductor filled with 20-mesh zinc has been found to offer little, if any, advantage in point of time, because of the extremely slow passage of the solution through the long, thin tube. The difficulty of preventing reoxidation was present here also.

This latter point, however, was successfully met by the simple device of letting the titanous solution run directly from the reductor into an excess of ferric solution previously placed in the receiving vessel. An ex-

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[1] *Trans. Am. Inst. Min. Eng.*, 1910, 793.

[2] *Orig. Comm. 8th Intern. Congr. Appl. Chem.*, 1, 445.

[3] *Am. J. Sci.*, [4] 25, 130, 343.

tension tube reaching nearly to the bottom of the receiver was used. The reduction of the Fe^{III} by the Ti^{III} is instantaneous and in place of titanous sulfate only the very stable ferrous sulfate comes into contact with the atmosphere.

The slowness and inconvenience of the long, narrow reductor still remained.

The zinc used was somewhat finer than is recommended by Shimer and Shimer, and to this may be due part of the difficulty, but none other being at hand, it was sought to improve matters by using a reductor of ordinary dimensions which could be heated continuously by means of a current of electricity circulated through a winding about the barrel of the instrument. This device proved entirely successful, not only titanic but also chromic salts being completely reduced in a few minutes.

The instrument is a reductor of the usual form, having a column 2.5 cm. in diameter by 20 cm. in height of coarse granulated zinc well amalgamated. The tube is wrapped with a few feet of resistance ribbon—iron wire would suffice—in series with a lamp or other resistance adapted to taking sufficient current from a lighting circuit to boil the contained solution.

To use the reductor, the stopcock at the bottom is closed, and the tube is partly filled with hot 5% H_2SO_4, which is followed by the solution to be reduced. A 2-holed rubber stopper, carrying a funnel tube with a stopcock and a small vent tube, is then placed in the top of the reductor and the contents are brought near to boiling and held there for 10–20 minutes. The internal pressure is then, by an obvious manipulation of the openings, allowed to force the charge into an excess of acidified ferric ammonium sulfate solution through a tube extending to the bottom of the vessel as before described. A tall narrow beaker may advantageously be used. More acid is then admitted and forced out as before. These operations are carried out without access of air to the space above the zinc. The washing is then completed with 1% H_2SO_4, with the top of the reductor open as usual. The reduced iron is titrated with $KMnO_4$ in the usual manner, and the titanium present calculated:

$$Fe^{III} + Ti^{III} = Fe^{II} + Ti^{IV}$$

The only thing to be guarded against is a tendency for a portion of the contents of the receiver to be sucked back into the reductor if the steam in the latter is allowed to condense during emptying. This offers no practical difficulty.

The solutions for reduction should contain about 5% free H_2SO_4. Much more than this causes too vigorous action.

The procedure for chromium solutions is identical with the above:

$$Fe^{III} + Cr^{II} = Fe^{II} + Cr^{III}$$

The method was checked up in the case of titanium by means of a standard solution prepared from potassium fluotitanate, K_2TiF_6, by fuming off with H_2SO_4. The TiO_2 content was determined gravimetrically by precipitation with NH_4OH with the precautions laid down by Bornemann and Shirmeister,[1] with the following results:

G. TiO_2 per cc. 0.01196, 0.01197, 0.01196.

10 cc. portions of this solution were then reduced and determined as described in the foregoing, giving

G. TiO_2 per cc., 0.01196, 0.01195, 0.01195.

The permanganate solution used was standardized against Mohr's salt.

For chromium, the standard solution was prepared by dissolving a weighed portion of pure fused $K_2Cr_2O_7$ and making up to a definite volume such that 1 cc. contained the equivalent of 0.01035 g. Cr_2O_3. This solution, analyzed by the reductor method in 10 cc. portions gave

G. Cr_2O_3 per cc., 0.01032, 0.01035, 0.01035.

The application of this method to the analysis of a mixture containing iron, chromium and titanium may be considered as an illustration.

The substance is brought into sulfate solution by known methods and made up to a definite volume. Iron is determined in an aliquot portion by titration after reduction in a reductor in the ordinary manner, with the important exception that Bi_2O_3 is added to reoxidize any reduced titanium and chromium.[2] Or the reduction may be effected with H_2S or SO_2 which have no action on Ti^{IV} or Cr^{III}.

A second portion is treated in the heated reductor in the manner described. The subsequent titration gives the permanganate equivalent of all three constituents combined.

The chromium alone is determined in a third portion by conversion to Cr^{VI} by boiling with ammonium persulfate and titrating in the usual manner with Fe^{II} and $KMnO_4$. Substituting the $KMnO_4$ equivalent for the Cr found, and adding to it that of the Fe, the Ti is then obtained by difference. Since the determinations upon which rests the result so obtained are not subject to significant error, the usual criticism of results by difference applies with a minimum of force, especially when one considers the well known difficulty of the separations involved in a direct determination of this metal in such combinations.

Practically any analysis involving these three metals can be readily handled so that a solution adaptable to the above procedure is obtained; in fact, it is generally easier than not so to handle it. Of other metals, tungsten, molybdenum and vanadium can be reduced by the treatment, but are easily removed in the preparation of the solution.

An exception to this generalization should perhaps be made in the case

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[1] *Metallurgie*, **7**, 711.

[2] Newton, *Am. J. Sci.*, [4] **23**, 365

of certain complex alloy steels, the application to which of the procedure described, while not discouraged, has not as yet been considered in detail.

Summary.

An oxidimetric determination of Ti and Cr, involving the use of an electrically heated reductor, is described, by means of which these metals may be determined easily and accurately, either alone or together with iron and other metals.

The writer wishes to express his appreciation of the services of A. Ortiz and also of H. B. C. Allison, who performed the test analyses cited and suggested the extension of the procedure to Cr.

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THE PERMANGANATE DETERMINATION OF IRON IN THE PRESENCE OF CHLORIDES.

BY O. L. BARNEBEY.

Received March 25, 1914.

Since the original proposal of the permanganate titration of iron by Marguerite,[1] the method has undergone various modifications. The majority of these changes were made to obviate the high results obtained by titrating in the presence of hydrochloric acid. This error was first pointed out by Löwenthal and Lenssen[2] and later by a number of authors.[3-26] Kessler[4] first called attention to the fact that considerable sulfuric acid, and still better manganese salts, greatly reduced the influence of the hydrochloric acid. Zimmerman[5] then proposed the use of manganese salts for this purpose, claiming as great an accuracy in hydrochloric as in sulfuric acid solutions. Reinhardt[7] next suggested the use of phosphoric acid also, for the removal of the color of ferric chloride to insure a better end point.

The permanganate method, used very largely to-day for the determination of iron in ores, in brief is as follows: Solution of the ore by heating with stannous chloride and hydrochloric acid, completion of the reduction by adding stannous chloride to the hot solution until colorless, dilution, addition of mercuric chloride to remove the excess of stannous salt, addition of the Zimmerman-Reinhardt solution (sometimes known as "preventive solution") containing sulfuric acid, manganese sulfate and phosphoric acid, and titration with permanganate, taking the first recognizable tint of color, permeating the entire solution for a short time, as the end point (inasmuch as the end point is somewhat unstable in the presence of chlorides).

The question which has concerned most of the authors quoted is: Does the Zimmerman-Reinhardt, or similar solution really prevent the action of hydrochloric acid? Birch[23] maintains that the method is only