ART. XXVIII.—*The Deportment of Titanium with reagents in Iron Ores containing Phosphoric Acid*; by E. H. BOGARDUS.

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THE injurious action of titanium upon iron when present in the metal in considerable quantity, and its frequent occurrence in nature, render it important that a reliable method for its detection be known, and that its presence or absence be proved in all analyses of ores.

During the summer of 1872, while engaged in the examination of some samples obtained in the mines of New Jersey, I encountered a difficulty, which I shall explain somewhat in detail. Subsequent experiments proved the presence of titanium, and that this substance had caused me my trouble. The deportment of the element was so different from what is taught in books of analyses, and from what I had previously observed, that it seemed to me that the usual directions given for its detection were faulty and liable to mislead the analyst. A more extended investigation served to strengthen this impression, and, in view of the importance of the subject, led to the preparation of the following paper.

Although it was not intended at that time to make complete analyses of the ores, it was thought important to test for titanium. To this end a sample was fused with bisulphate of potash and digested in cold water. The dissolved substance was then filtered and the clear liquid treated with sulphuretted hydrogen to effect the reduction of the iron. This should have caused no precipitate of titanium under ordinary circumstances. Sulphur, of course, separated in proportion to the iron reduced, and was removed by filtration. The liquid was now boiled, and as it remained clear, even after long heating, the absence of titanium might have been regarded as demonstrated. The examination, however, did not stop here: it was decided to test the sulphur remaining on the filter. On burning this precipitate a residue was obtained amounting to nearly six centigrams, although but a gram of ore had been

taken for the examination. As sulphur would have been vaporized by the heat, the burning, of course, proved the presence of some other body. As the absence of zinc and the members of the fifth and sixth groups had been proved, the only elements supposed to be precipitable by sulphuretted hydrogen under the existing conditions, the supposition was that a mistake had occurred. The experiment was, therefore, repeated and with identical results. As it now seemed certain that sulphuretted hydrogen had caused a precipitate, the next step made was to determine its character. The substance was white both before and after heating, and resembled closely sulphide of zinc. After burning, it held no sulphur. The absence of color and sulphur would alone have seemed sufficient proof of the absence of the fifth and sixth groups, without the concurring evidence as afforded by the previous regular qualitative tests. But since it could not be denied that a substance had formed and its formation seemed an anomaly, it was determined to examine again and this time for all bases without exception. It would require too much time, and would serve no useful purpose, to enter into a minute description of the course taken in this examination, so I will confine myself to a statement of a few of the properties as developed during the experiments. After burning the precipitate and fusing it in bisulphate of potash, it was insoluble in water. It was sparingly soluble in hydrochloric acid immediately after precipitation with sulphuretted hydrogen, but it could be dissolved after repeated boiling in fresh quantities of acid. Fusion in carbonates of the alkalis rendered it soluble in hydrochloric acid. It was insoluble or nearly so in boiling solution of potash; precipitated with difficulty or not at all in slightly acid solutions. It colored microcosmic salt brown, gave a transient green color to the blowpipe flame, fused to a black non-magnetic globule on heating on charcoal, and when dissolved in hydrochloric acid imparted a brown tint to turmeric paper like that produced by boracic acid. The effect on turmeric paper led to the supposition that the substance was partly zirconia. The thought at length suggested itself that as there was no sulphur in the precipitate, its formation might be due to a reducing action. Sulphurous acid being a powerful reducing agent, it was determined to substitute this for sulphuretted hydrogen. A sample of ore was fused as at first in bisulphate of potash; then dissolved, filtered, and the reducing gas passed through the liquid. A red coloration at first appeared, followed by a white precipitate like that obtained in the first instance. A quantity of ore was now digested in hydrochloric acid and filtered to separate the insoluble matter. After nearly neutralizing the free acid with ammonia, acetate of ammonia was

added in excess, and then acetic acid in large quantity. On passing sulphuretted hydrogen a white precipitate was again obtained. This experiment was repeated several times with identical results, proving that the substance would form in a solution holding free acetic acid. The precipitate was again subjected to a qualitative examination and this time with success. Previously no search had been made for acids: it was now decided to test for them. Phosphoric acid was soon found and the true character of the substance was easily determined. The precipitate was fused in carbonates of soda and potash and digested in water. The phosphoric acid was all dissolved and was detected with molybdate of ammonia. The nearly white residue was proved to be a mixture of titanium and iron. One-half gram of the ore was mixed with an equal weight of an ore holding a large quantity of titanium. The mixture was fluxed in bisulphate of potash, and finally subjected to the action of sulphuretted hydrogen. A precipitate weighing six centigrams was obtained. The sample first examined could give only two and a half centigrams of precipitate. This experiment was followed by the regular tests for titanium, and its presence was soon demonstrated. Rutile was now powdered and mixed with phosphate of soda and an ore free from titanium. After fusion with bisulphate of potash and digestion in water, sulphuretted hydrogen gave a precipitate as in the previous trials. As it now seemed proved that sulphuretted hydrogen could precipitate titanium, it became interesting to know whether the precipitate formed was definite in its composition. It was intended to pursue this question to a satisfactory solution if possible, but owing to the pressure of other matters but little was done: too little to justify the assertion that the precipitate was a definite compound. Several experiments were subsequently made, on mixed samples of rutile and an ore and phosphate of soda, and a precipitate was obtained in every instance with sulphuretted hydrogen. In one case the phosphate of soda was dissolved in water and added to the fused rutile and ore. Rutile was now fused in bisulphate of potash and digested in water; after filtering, sulphuretted hydrogen gave no precipitate. This trial was made to determine whether iron was necessary to precipitation; the result seemed to demonstrate the necessity of its presence and that the formation of a precipitate is dependent upon the reduction of iron. The deportment of titanium with phosphoric acid led to the thought that possibly it might be employed as an agent in the quantitative separation of the phosphorus in iron ores. No experiments were made with a view to the settlement of this question. In all the co-precipitations of titanium and phosphoric acid, the latter was present in

excess. It is possible that titanium in excess would have prevented precipitation with sulphuretted hydrogen. The subject seems worthy of an investigation. Let us now pass in brief review over the ground we have traversed, and endeavor to see what light has been thrown upon the properties of titanium and whether the method of its detection, by fusion with bisulphate of potash, as given in books, is all that could be desired, and whether it could not occasionally mislead the analyst. First, the properties of titanium. It was found that it would not precipitate readily in an acid solution on boiling. Phosphorus seemed to hinder, if not to entirely prevent, precipitation; so this method, which is much employed, is faulty. Indeed, this was known before, for some works of analyses tell us that zirconia at least will prevent the separation of titanium from boiling liquids. 2d. We find that titanium colors turmeric paper a brown, or nearly orange color, a fact before known but not generally mentioned in analytical works. 3d. Sulphuretted hydrogen throws down titanium, although no books seem to teach it. Let us now imagine the case of a student testing ores for titanium. He fuses his sample in bisulphate of potash and digests it in water: he filters, and passes sulphuretted hydrogen through the liquid. Sulphur of course separates and gives the solution a milky appearance; he regards this sulphur free from titanium. As the milky appearance would render it impossible to see whether a precipitate formed on boiling, he decides to filter and thus render the liquid clear. On boiling no precipitate forms. The titanium has been thrown away with the sulphur, and the analyst has formed a false idea of the composition of his sample. It is plain, then, in case of filtration, after passing sulphuretted hydrogen, that the sulphur should be examined, provided titanium be not found on boiling the liquid.