ANALYTICAL PROCEDURE FOR THE DETERMINATION OF TITANIUM AND IRON IN TITANIFEROUS ORES*

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INTRODUCTION. The analysis of titaniferous ores offers many problems. There appear to be difficult or objectionable features in all published procedures. The procedures given herein are no exception but possess certain advantages over others when applied to Oklahoma ores.

The titanium minerals are essentially oxygenated compounds and are often very difficult to decompose and put into solution. As a matter of fact, "excepting hydrofluoric, the acids attack them only imperfectly"[2] Further, they are often intimately mixed or associated with other minerals difficult to dissolve. For the purpose of analysis it is usual to resort to pyrosulfate fusion, followed by an alkali fusion of any undecomposed or insoluble material. By whatever method obtained, solutions of titanium salts, with the possible exception of the oxalates[1], are more or less unstable due to their tendency to hydrolyze. In order even partially to prevent hydrolysis of titanium chloride and sulfate solutions it is necessary to maintain high acid concentrations and to keep temperatures low. Generally, with low acid concentrations and especially with application of heat, hydrolysis will occur. Much of the titanium will separate as relatively inert dioxide. Obviously, there are serious objections to any analytical procedure encountering such conditions.

The procedure presently followed in the laboratory of the Oklahoma Geological Survey for the determination of titanium, "total iron", and ferrous iron is not claimed to be original. Modification and adaptation of known methods and equipment are used which seem best suited to conditions found in working with Oklahoma ores.

PREPARATION OF SAMPLE. The material is reduced to pea size by crushing. After quartering and re-quartering to an acceptable quantity, one portion is reduced to minus 100 mesh, using a power-driven grinder with agate mortar and pestle, and a second portion is further reduced by crushing only, in order to prevent any oxidation of ferrous iron by heat generated in grinding[4]

APPARATUS. Special apparatus used in making the analyses consists of (1) a solutionizing assembly, (2) a reduction assembly, and (3) a titration assembly. These, together with a cylinder of carbon dioxide and a purification train, are the essential equipment. Figure 1 shows on the right a 300 ml. Erlenmeyer flask with a three-hole rubber stopper. One hole is fitted with a glass tube that extends to the bottom of the flask and is bent at right angles, ending in a curved capillary tip. This tube is for delivery of CO_2 in a fine stream at an angle with the wall of the flask. The CO_2 is used for two purposes: to assure an inert atmosphere in the flask, and to cause agitation of the contents. For use as a "solutionizing assembly", one hole is fitted with a glass tube approximately 18 inches in length which serves as an air-cooled condenser, and the third hole is plugged with a piece of glass rod. For use as a "titration assembly" the plug is removed and the glass tube replaced by a burette.

On the left in Figure 1 is shown another 300 ml. Erlenmeyer flask with a two-hole rubber stopper. The holes are fitted with short pieces of glass tubing, to one of which is attached a rubber Bunsen valve which will allow the escape of gas under pressure but will not allow air to enter even though the pressure inside the flask is less than the atmospheric pressure, and on the other is a short piece of rubber tubing on which is a metal clamp. This is the "reduction assembly" when a zinc-amalgam coil has been placed in the flask.

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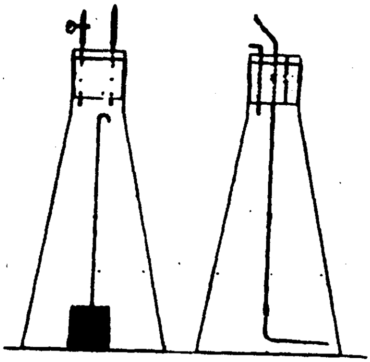

FIGURE 1. Reduction Assembly, at left. Solutionizing Assembly, at right.

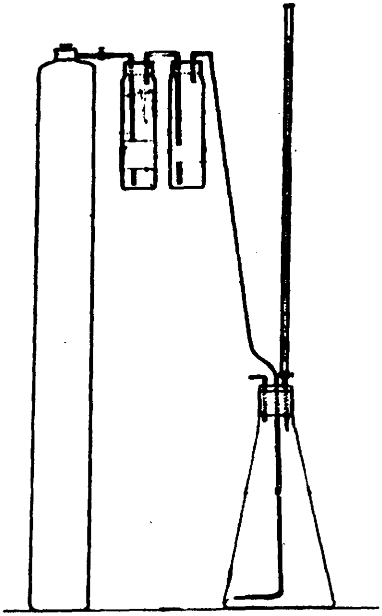

FIGURE 2. Titration Assembly and CO_2 Train.

Figure 2 shows the "titration assembly" connected to the CO_2 tank and purification train. The tank is equipped with a needle valve for control of the gas flow, an absorption bottle to remove carbon monoxide and oxygen, and a wash bottle. The absorption bottle contains ammoniacal copper chloride solution and copper wire[3]. The wash bottle contains 10% sulfuric acid solution to absorb ammonia and prevent its being carried over into the flask.

REAGENTS. Potassium permanganate solution, 0.1 and 0.025 N; Methylene blue, 0.5% aqueous solution; O-Phenanthroline ferrous complex, 0.025 M; Sulfuric acid, conc., 10% by volume, and 20% by volume; Boric acid; Hydrofluoric acid, 50% HF.

DECOMPOSITION OF SAMPLE AND PREPARATION OF SOLUTION. For the determination of titanium and "total iron", a 0.5 gm sample is fused in a platinum crucible with 5 gm of sodium carbonate. The melt is cooled and dissolved in sulfuric acid. The quantity of acid is calculated from the amount necessary to combine with the oxides present, neutralize the alkali, and furnish a minimum excess acid strength of 10% by volume when diluted to 150 ml. The alkali fusion is employed in order to convert refractory titanites, chromites, and silicates into compounds decomposable by sulfuric acid.

For the determination of ferrous iron, a 0.5 gram sample is weighed into the flask of a "solutionizing assembly". All air is swept out with CO_2. Continuing the flow of CO_2, 150 ml 10% sulfuric acid and 10 ml hydrofluoric acid are added. The stopper is forced firmly into the neck of the flask. The flow of CO_2 is adjusted to give motion and agitation to the contents of the flask, and the assembly is set on the steam bath. As much as 24 hours but usually less, may be required for maximum decomposition. The temperature in the flask will remain between 80° and 85°C, the flow of gas having a cooling effect.

DETERMINATION OF COMPOSITION. One gm samples are ignited in porcelain crucibles at 1000°C for 16 hours under oxidizing conditions. The gain, in weight if any, supplies information on the probable ferrous iron content. The loss, if any, may indicate the presence of altered minerals such as hydrous iron oxides.

TITANIUM AND "TOTAL IRON". The sample having been decomposed and put into solution as under (A) above, is placed in a flask of a "reduction assembly", 3 drops of methylene blue solution added, the zinc-amalgam coil inserted, and the stopper forced firmly into the neck of the flask. The Bunsen valve and clamp are checked to see that they are in good working order. The flask and contents are placed on the hot plate, and a strong reaction maintained between the solution and the coil until the color of the methylene blue disappears and for thirty minutes additional to assure complete reduction of all reducible matter. On removal from the hot plate, the flask is connected to the CO_2 supply by the clamped rubber tube and the gases in the flask replaced with CO_2. Continuing the flow of CO_2 the stopper is cautiously removed, the coil washed down with 10% sulfuric acid and removed, and the stopper immediately replaced by the "titration assembly" stopper and the burette inserted. With a controlled flow of CO_2 to give the proper degree of agitation, 0.025 N permanganate solution is run in until the first indications of return of the blue color. For best results the temperature should not fall below 60°C; below 60°C the indicator is sluggish. The permanganate consumed is calculated to its equivalent as TiO_2.

The temperature is reduced to below 25°C. The stopper is momentarily raised to permit introduction of 3 drops of O-phenanthroline ferrous complex solution, the flow of CO_2 being maintained the while, and titration continued with 0.1 N permanganate solution until the color changes from reddish to bluish grey. Above 25°C the indicator is unstable. The permanganate consumed in this titration is calculated to its equivalent as iron, and recorded as "total iron", being iron present in both ferrous and ferric condition. It will be observed that this procedure is a modification of that of Shippy[4].

The sample having been put into solution as under (B) above, the flow of CO_2 is continued, the flask is cooled to below 25°C, the condenser tube and plug are removed, and replaced by a burette and vent tube, 6 grams of boric acid are cautiously added for the purpose of complexing the fluorides present, after which the solution is titrated with 0.025 N permanganate solution. It may be possible to titrate without the aid of the indicator, relying on the pink of excess permanganate, but with weak permanganate the indicator seems preferable. The permanganate consumed is calculatd to its quivalent as Feo.

COMMENTS. Complete solution of chromite is not always obtained by the hydrofluoric-sulfuric treatment. Obviously any ferrous iron remaining in suspension as chromite will not be found.

True values for titanium and iron can be obtained only by a complete analysis of the material, whereby the amount of certain minor constituents such as vanadium and chromium may be used in calculating corrections to be applied to the values found in the foreging procedure.

Titaniferous ores are usually quite complex, as is indicated by petrographic examination. The same fact may be inferred from the analysis of an Oklahoma ore as given in Table I.

TABLE I

TiO_2	16.54 %	"total iron" Fe	54.5 %	FeO	14.7 %
Cr_2O_3	0.40 %	V_2O_3	0.25%	Fe_2O_3	60.8 %
Al_2O_3	4.00 %	SiO_2	1.10%	CaO	0.05%
MgO	2.60 %	MnO	0.37%	NiO	0.02%
P_2O_5	0.002%	S	0.01%	(NaK)O	n.d.

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