

following table. The substance is richer in formate than the one pre-

Fe. Percent.	CHO <sub>2</sub> Per cent.	
53.0	17.2	
51.6	18.5	Required for $\left[ \begin{array}{c} (\text{CHO}_2)_2 \\ \text{Fe}_3 \text{ OH} \\ \text{O}_3 \end{array} \right]$ , Fe 51.9 per cent., CHO <sub>2</sub> 27.9 per cent.
50.7	19.3	

cipitated hot. It corresponds somewhat closely in composition to the formula of a basic diformate, but I incline to the belief that it is a mixture of the basic monoformate with a small quantity of some formate richer in formic acid.

### Summary.

1. The iron group may be precipitated as basic formates, which filter somewhat more readily than the basic acetates.
2. The presence of iron is necessary for the precipitation of chromium.
3. It was found impossible by any of the methods heretofore described to prepare normal ferric formate. In its place was always obtained a good crystalline precipitate corresponding to the formula  $\text{Fe}_3(\text{CHO}_2)_7(\text{OH})_3$ .
4. The basic formate precipitated under the usual conditions possesses

a composition expressed by the formula  $\left[ \begin{array}{c} \text{Fe}_3 \text{ CHO}_2 \\ (\text{OH})_2 \\ \text{O}_3 \end{array} \right]$

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## A RAPID AND ACCURATE METHOD FOR THE DETERMINATION OF TITANIUM.

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Having a number of determinations of titanium in rutile and iron ores to make and failing to obtain consistent results by use of the common methods the authors proceeded to investigate for a shorter yet accurate process for this determination. Low's method<sup>1</sup> adapted from Blair gives good results, but requires too much time for the ordinary analysis. This method was used in checking three series of analyses. Gooch's method was not tried as it seemed to have the same disadvantage as the other methods—requiring too much time to obtain a pure product of weighable titanium oxide.

Methods depending on the precipitation of titanous acid in boiling solutions containing sulphurous and sulphuric acids gave low results. Those requiring SO<sub>2</sub> or H<sub>2</sub>S reduction of the iron and precipitation of the titanium with ammonia or by boiling with sodium or ammonium acetate and acetic acid were found to give high results when a large excess of iron was present, and required repeated treatments to completely remove the latter element.

<sup>1</sup> Low's "Technical Analysis of Ores," p. 189.

This accords with the results of Blair,<sup>1</sup> Fresenius,<sup>2</sup> and others. Pisani's<sup>3</sup> volumetric method, modified by Wells and Mitchell,<sup>4</sup> reducing the titanium from  $TiCl_4$  or  $Ti(SO_4)_2$  by zinc in the presence of free acid and titrating with potassium permanganate in an atmosphere of carbon dioxide failed to give accurate results. In no case where considerable titanium was present was the reduction absolutely complete and frequently the results were from 5–10 per cent. low after prolonged reduction by the zinc. This is in accordance with the published work of Wells and Mitchell<sup>5</sup> on the application of this method.

Rothe's method<sup>6</sup> for the removal of the iron from titanium in the determination of the former, used likewise by Noyes, Bray and Spear<sup>7</sup> to separate titanium and zirconium from iron and thallium in their System of Qualitative Analysis finds application in removing most of the iron quickly. The method attributed to Ledebur by Classen<sup>8</sup> for pig iron analysis will not give good results due to the presence of titanium in the silica and graphite which is discarded, the solubility of titanous acid in hydrochloric acid, and the contamination of the final product by foreign elements such as aluminium.

The method as outlined below is based on the volatilization of the silica by hydrofluoric acid in the presence of sulphuric acid, evaporation to dryness and fusion with sodium carbonate and a little sodium nitrate to convert the iron and titanium to insoluble ferric oxide and sodium titanate, extraction with hot water to remove the soluble phosphates, sulphates and aluminates; solution of the ferric oxide and sodium titanate in hydrochloric acid, extraction of ferric chloride with ether; reduction of slight traces of iron with sulphur dioxide; precipitation of the titanous acid by boiling in acetic acid solution, filtration and ignition to titanium oxide (or colorimetric). (If the directions as given are strictly followed usually the sulphur dioxide reduction may be omitted as the iron will have been completely removed.)

The weighed sample in a platinum crucible is moistened with water, 5–10 drops concentrated sulphuric acid, and 1 cc. of hydrofluoric acid are added, and the mixture heated on an asbestos hot plate until cessation of sulphur trioxide fumes. Five or ten grams of sodium carbonate and a little sodium nitrate are added and the mixture fused at least 30 minutes. The crucible and cover are cooled, placed in a beaker, covered with hot

<sup>1</sup> Blair's, "Chem. Anal. of Iron," p. 180.

<sup>2</sup> Fresenius-Cohn, *Quant. Chem. Anal.*

<sup>3</sup> *Ibid.*, Vol. I, 285.

<sup>4</sup> THIS JOURNAL, 17, 878.

<sup>5</sup> *Loc. cit.*

<sup>6</sup> *Mitt. Königl. tech. Vers.*, 10, 132; *Stahl und Eisen*, 12, 1052; 13, 333.

<sup>7</sup> THIS JOURNAL, 30, 515.

<sup>8</sup> Classen's, "Ausgewählte Methoden der Anal. Chemie," p. 501.

water and heated until the melt is disintegrated. Ferric oxide and sodium titanate are left in the residue insoluble in hot water. The crucible is removed, washed and any adhering particles of ferric oxide and sodium titanate are dissolved out with hot hydrochloric acid (sp. gr. 1.11). These solutions are saved. The residue in the beaker is filtered and washed with hot water. The filter is perforated and the residue carefully washed down into a clean beaker with hydrochloric acid (sp. gr. 1.11). The hydrochloric acid washings from the platinum crucible are transferred to the beaker and the whole heated on the hot plate until solution is complete and volume is reduced to 15-20 cc. The solution is cooled, 2 cc. of concentrated hydrochloric acid added, and transferred to a separatory funnel, the beaker being rinsed with hydrochloric acid (sp. gr. 1.11). An equal volume of ether, which has been previously shaken with concentrated hydrochloric acid, is added to the solution, a rubber stopper is inserted in the top, the funnel is inverted, the stopcock opened and the whole thoroughly shaken. The stopcock is then closed and the funnel placed in an upright position and allowed to stand 10 minutes. The aqueous layer is drawn off into another separatory funnel. The ether is rinsed twice by shaking well with 5-10 cc. portions of hydrochloric acid (sp. gr. 1.11) and the washings added to the aqueous solution. (The ether is run off into an ether residue bottle and saved for purification.) The treatment with ether is repeated two or three times until the ether layer no longer shows any greenish tinge due to the presence of dissolved iron. The aqueous solution is then transferred to a beaker and 3-5 cc. of hydrogen peroxide added. If the solution does not develop a fairly intense color the titanium may be determined colorimetrically by the method given below.

If an intense color develops the solution is heated to expel dissolved ether, 10 cc. of concentrated sulphuric acid are added and the solution evaporated to sulphur trioxide fumes. The cooled solution is diluted to about 100 cc. (any platinum present should be precipitated by hydrogen sulphide at this point) and the solution nearly neutralized with ammonia. One or 2 grams of ammonium bisulphite are added and the solution warmed on the hot plate for half an hour. Ten to 15 grams of ammonium acetate are added and 5-10 cc. of glacial acetic acid and the solution boiled for 15 minutes. Filter. The precipitated titanate is filtered off washed with dilute acetic acid (not over 11 per cent.), ignited and weighed as titanium oxide.

In case the hydrogen peroxide test as performed above indicates the presence of only a small amount of titanium the quantity may be determined colorimetrically. Heat the solution to expel dissolved ether, cool, transfer to a Nessler's tube, treat with 4-5 cc. of hydrogen peroxide, dilute to 100 cc. and determine by comparison with measured quantities

of a standard solution of titanous acid in hydrochloric acid, which have been subjected to the same peroxide treatment. This comparison can be most conveniently carried out by adding the standard solution, drop by drop from a burette, to a Nessler's tube containing hydrogen peroxide and hydrochloric acid and made up to near the 100 cc. mark. The solution should be agitated from time to time and the process continued until an equivalent color is developed.

In following out this method as outlined three ores were used. Sample A was a sample of rutile from Kahibaum, sample B was a specimen of concentrates from a Virginia ore, and sample C was a titanium iron ore from Lower Canada. These ores were analyzed by the method given above and the results checked by use of the method proposed by Low. The results obtained are tabulated in the following table.

Sample.	Method.	Wt. $\text{TiO}_2$ $\text{Fe}_2\text{O}_3$		Final wt. $\text{TiO}_2$ .	Per cent. $\text{TiO}_2$ .	Average per cent.
		Wt. Samples.	1st ppt. by Low. <sup>1</sup>			
A...	Authors' method....	0.2		0.1652	82.60	82.58
				0.1650	82.50	
				0.1652	82.60	
				0.1653	82.65	
				0.1651	82.55	
	Low's method.....	0.2	0.1782 0.1694	0.1652	82.60	82.67
				0.1655	82.75	
				0.1776	88.80	
				0.1774	88.70	
				0.1771	88.55	
B...	Authors' method....	0.2		0.1772	88.60	88.55
				0.1770	88.50	
				0.1770	88.50	
	Low's method.....	0.2	0.1772 0.1770	0.0785	15.70	15.67
				0.0785	15.70	
				0.0781	15.62	
C...	Authors' method....	0.5		0.0783	15.66	15.67
				0.0783	15.66	
	Low's method.....	1.0	0.1618 0.1708	0.1552	15.52	15.51
				0.1550	15.50	

In a preliminary effort to show the quantitative nature of the ether separation the following experiments were performed: I. A solution of titanous acid in hydrochloric acid was standardized by precipitation with ammonium hydroxide and ignition to titanium oxide. II. Blanks were run, carrying 10 cc. portions of the titanium solution through three ether separations with final precipitation with ammonium hydroxide. III. Separations were run by mixing 10 cc. portions with 5 cc. of a saturated ferric chloride solution and subjecting the mixture to the regular ether treatment with sulphur dioxide reduction and ammonium acetate precipitation.

<sup>1</sup> Using Low's method whenever iron was present it was found necessary to refuse and reprecipitate to free the titanium oxide from ferric oxide.

I (a) 0.1140	II (a) 0.1142	III (a) 0.1141
(b) 0.1139	(b) 0.1144	(b) 0.1140
		(c) 0.1141

It is suggested that for the analysis of pig iron, steel, etc., a 5-10-gram sample be dissolved in 30-40 cc. of concentrated hydrochloric acid to which 4-5 cc. concentrated nitric acid has been added, and the solution evaporated to the consistency of sirup. Add 1-2 cc. of concentrated hydrochloric acid, take up with 20 cc. of hydrochloric acid (sp. gr. 1.11), and filter. Transfer the filtrate to a separatory funnel and the residue to a platinum crucible.

After one treatment with ether as given above, the aqueous solution should be treated with ammonia, the precipitate filtered out and added to the residue in the platinum crucible. Ignite filter paper, treat with hydrofluoric acid, fuse, and complete the determination as previously given.

We note that in the original colorimetric work of Weller,<sup>1</sup> as well as in all subsequent modifications, the titanium was oxidized in the presence of sulphuric acid. For the sake of comparison equivalent solutions of titanium in sulphuric and in hydrochloric acid were prepared. We found that the color developed by oxidation was fully as intense and stable, in hydrochloric as in sulphuric acid. Inasmuch as solutions containing 1 mg. or more of titanium developed a somewhat higher color with hydrochloric acid it is advisable to use a standard solution of titanium in hydrochloric acid for the comparison.

Observing the aqueous titanium solution in the ether extraction to be colorless if peroxide-free ether is used led us to doubt the formation of a "yellow-white compound" with ether described by Rosenheim and Schütte.<sup>2</sup> These authors write: "The yellow-white, very indistinctly micro-crystalline mass, which remains after the action of hydrochloric acid and ether on titanium hydroxide, was almost completely soluble in cold water and precipitated gelatinous titanous acid on boiling." Treating titanium hydroxide in all degrees of hydration with several proportions of hydrochloric acid in ether gave no color mentioned above provided the last trace of peroxide was removed from the ether. If even a small amount of peroxide was present, Rosenheim and Schütte's observations were confirmed.

### Conclusions.

1. The volumetric method based on the reduction of titanium to the tri-valent state and oxidation with permanganate gives low results.
2. With the sulphur dioxide reduction when considerable iron is present the titanium product is usually contaminated with some iron.

<sup>1</sup> *Ber.*, 15, 2593.

<sup>2</sup> *Z. anorg. Chem.*, 26, 241.

3. The ether separation removes practically all the iron from the titanium very quickly.

4. Refusion of the ignited product with sodium carbonate for purification, which requires considerable time, is never necessary by use of this method. The final product is pure, unless zirconium is present, in which case this element is removed by the usual phosphate precipitation.

5. This method combines the colorimetric and gravimetric determinations and the color comparison is made in solutions always totally free from iron. For convenience hydrochloric rather than sulphuric acid solutions of titanous acid are used.

6. The method is accurate and not long.

7. Rosenheim and Schütte's yellow compound probably owes its color to the presence of peroxides in the ether used.

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## APPARATUS FOR THE DETERMINATION OF ARSENIC.

BY OTIS D. SWETT.

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The many existing forms of apparatus for the determination of arsenic which give trustworthy results appear to have left little to be sought for with regard to this most essential feature. The more or less complex construction of these forms, however, together with the sources of error which usually accompany such construction, seem to justify an attempt to devise an apparatus for arsenic determination which, besides yielding accurate results, shall comprise fewer parts than are found in the other forms, and shall be compact and portable.

With these points in mind, an apparatus has been devised which is illustrated in the accompanying drawing.<sup>1</sup>

*A* is a round wooden base with a central depression and three vertical lugs which form an extension of the sides of the depression.

*B* is a glass vessel, 4 cm. outside diameter and 14 cm. long, with flat closed bottom, supported by the base *A* in the depression between the vertical lugs. The vessel *B* is provided with a lower side tube *b*, projecting beyond the base *A* between the vertical lugs, and with the upper side tube *b'*.

*C* is an inner tube, 18 mm. outside diameter, closed at its lower end, enlarged conically at its upper open end, rolled out and sealed to the top of the vessel *B*, which is closed in to meet it, and then ground on its inner surface to receive a stopper.

*D* is a hollow stopper with dome-shaped closed top, tapering to the other end, which is open, and ground to fit the neck of the inner tube *C*.

<sup>1</sup> Glass work by Mr. Edw. O. Sperling, Bureau of Standards.