A NEW METHOD FOR THE VOLUMETRIC ESTIMATION OF CHROMIUM, VANADIUM, AND IRON, IN PRESENCE OF ONE ANOTHER.

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ATTEMPTS have been made to apply to the estimation of chromium and vanadium the method of reducing with zinc and hydrochloric acid, subsequently titrating with standard methylene blue solution, as used by Knecht and Atack for the estimation of molybdenum (ANALYST, 1911, **36**, 98), and by Atack for the estimation of tin in presence of antimony (*J. Soc. Dyers and Col.*, 1913, **29**, 9). It was not found possible to obtain a process for the estimation of vanadium based on the oxidation of VCl_2 to VCl_4 by methylene blue, owing to the slow rate at which the VCl_3 first formed is oxidised to VCl_4; indeed, the VCl_3 stage could be roughly distinguished by the change from rapid to slow disappearance of the methylene blue colour. The results obtained made it evident that the state of oxidation represented by V_2O_4 is stable in presence of methylene white, and the method now suggested is based on the oxidation of the leuco-dyestuff (methylene white) by means of vanadate (V_2O_5), resulting in the formation of methylene blue and V_2O_4. The amount of dyestuff so formed is then estimated, and corresponds to the oxygen available in the following equation:

$$2V_2O_5 = 2V_2O_4 + O_2.$$

Similarly, chromium cannot be estimated by reduction to chromous chloride, owing to the unstable character of this compound even in presence of a large amount of hydrochloric acid, but it has been found possible to use quantitatively the reduction of chromates to chromic salts on adding to methylene white:

$$4CrO_3 = 2Cr_2O_3 + 3O_2.$$

This method of oxidising a leuco-compound and estimating the dye produced is also available for the estimation of ferric salts, which are quantitatively reduced by methylene white to ferrous salts, and it has been found possible to combine the processes into a method for the estimation of chromium, vanadium, and iron, in presence of each other. In estimations in which leuco-methylene blue is used, nitric acid must not be present in the solution.

A convenient strength for the standard dyestuff solution is 4 grms. of fairly pure methylene blue (hydrochloride free from zinc) per litre. This approximately $\frac{N}{50}$ solution is readily standardised by one of the methods described elsewhere by the present author (*loc. cit.*), according to the reagents available. The method in which pure potassium chlorate is employed as the standard is to be recommended, a process identical with that described below for the estimation of chromate. A known volume of the standard methylene blue solution is heated to boiling with dilute hydrochloric acid in a current of carbon dioxide, and is then titrated whilst warm with titanous chloride solution until colourless. By this titration the titanous chloride solution is standardised, and the methylene white solution in the flask is ready for the addition of the oxidising agent to be estimated, standardisation and estimation being thus effected in the same flask. It is essential that an excess of methylene white be present to prevent the formation of chlorine and the consequent destruction of some of the methylene blue. Moreover, all methylene blue titrations must be carried out in an atmosphere of carbon dioxide, and in warm solution (over 40° C.) in order to obtain a sharp end-point. On account of the high tinctorial power of the methylene blue, the end-point is quite sharp, even if $\frac{N}{500}$ solution of the dyestuff and of titanous chloride are employed.

Estimation of Chromium.—The chromium salt is converted into chromate by oxidising with sodium peroxide, boiling to destroy the excess of the sodium peroxide, and then adding an aliquot portion of the chromate solution so obtained to a solution of methylene white prepared as above. The methylene blue so formed is estimated by titration with titanous chloride. The method has been tested on the purest Kahlbaum potassium dichromate, of which 1·3674 grms. were taken, dissolved in water, reduced with sulphur dioxide in presence of sulphuric acid, and made up to a litre after oxidising with sodium peroxide, the excess of which was destroyed by boiling. Fifty c.c. of standard methylene blue (1 c.c. = 0·00018 grm. oxygen) required 69 c.c. of titanous chloride, and on addition of 25 c.c. of the chromate solution further required 42·15 c.c. of titanous chloride for the methylene blue so formed. Addition of a further 25 c.c. of the chromate solution produced methylene blue equivalent to 42·2 c.c. of titanous chloride. One hundred and four c.c. of chromium are equivalent to 48 c.c. of oxygen. Thus, according to this method the sample contained 99·9 per cent. $K_2Cr_2O_7$.

Chromium in Presence of Iron.—Solutions containing iron and chromium are oxidised with sodium peroxide, boiled to destroy the excess of this reagent, and the precipitate dissolved by addition of dilute sulphuric acid. The solution is then made up to a known volume, and an aliquot portion added to methylene white solution, titration with titanous chloride then giving iron as ferric salt plus chromium as chromate. The iron is estimated by boiling a known volume of the solution with concentrated hydrochloric acid until the chromate has been completely reduced, making up to a known volume, and adding to methylene white. The method gave very satisfactory results with mixtures of standard iron alum and potassium dichromate. (See complete table later.) The method is available for the analysis of ferrochrome and of chromium steel. The powdered ferrochrome or chromium steel in the form of fine drillings are fused with caustic soda and sodium peroxide, and the melt extracted with water. The ferric hydroxide may be filtered off and the chromate estimated in the filtrate by addition to methylene white, or the iron and chromium may both be estimated by the process described above, in which case the chromium is determined by difference. The results of analyses of ferrochrome obtained by these processes agreed to within 0·2 to 0·3 per cent. on the chromium found.

Estimation of Vanadium.—The process employed is identical with that described above for chromium, oxidation being effected by sodium peroxide. The method has been tested on a pure (Kahlbaum I) ammonium metavanadate, NH_4VO_3, which should contain 77·8 per cent. V_2O_5. The sample was found to contain 77·6 per cent. V_2O_5.

Vanadium in Presence of Iron.—The process employed is similar to that used for the estimation of chromium in the presence of iron, the vanadium being estimated by difference. The method was tested on mixtures of known volumes of standard iron alum and ammonium vanadate solutions, and gave satisfactory results. (See complete table later.)

Chromium, Vanadium, and Iron.—It has been found possible to apply the above methods to the estimation of chromium, vanadium, and iron, in solution. The solution is oxidised with sodium peroxide, boiled, and made up to a known volume after addition of dilute sulphuric acid. (1) A suitable volume of the solution is added to methylene white, the methylene blue formed being titrated with titanous chloride. This gives the amount of chromate, vanadate, and ferric salt present. (2) Another portion is evaporated with concentrated hydrochloric acid to reduce the chromate and vanadate, the ferric salt remaining being estimated by addition to methylene white solution. (3) Finally vanadium, together with ferric salt, are estimated by reduction of a fresh portion of the solution with sulphur dioxide, boiling for a few moments, and then further replacing the sulphur dioxide by passage of a current of carbon dioxide through the liquid for a short time. There is no necessity to attempt a complete removal of the sulphur dioxide in this manner, as the solution is next oxidised with permanganate until it acquires a pink tinge, made up to a known volume, and the vanadate *plus* ferric salt estimated by addition of an aliquot portion to methylene white. The following results were obtained, using standard iron alum, ammonium vanadate, and potassium bichromate solutions:

	Found. Grm.	Present. Grm.
Vanadium	0·01750	0·01752
Chromium	0·00606	0·00604
Iron	0·01486	0·01483
Vanadium	0·01747	0·01752
Chromium	0·02413	0·02414
Iron	0·00745	0·00742
Vanadium	0·01776	0·01773
Chromium	0·01045	0·01050
Iron	0·01856	0·01850

In the analysis of chromium vanadium steel by these methods, the iron must be removed as hydroxide and estimated after solution in hydrochloric acid. It has been found possible to obtain a complete separation of the iron by fusing fine drillings of the steel with caustic soda and sodium peroxide. The melt is extracted with water, the whole being digested on a water-bath for some time, and then filtered through hardened filter-paper, finally washing with hot water. The filtrate contains the whole of the vanadium and chromium in the condition of vanadate and chromate, which are estimated by addition to methylene white of a portion of the solution. Another portion of the solution is acidified with sulphuric acid, filtered to remove silica if precipitated, reduced with sulphur dioxide, and then boiled for a short time. A current of carbon dioxide is passed through the solution, which is then oxidised with permanganate solution. A portion of this oxidised solution is added to methylene white to estimate the vanadium present. Fairly concordant results were obtained in three estimations of chromium and vanadium in a sample of steel:

	1.	2.	3.
Vanadium, per cent.	0·538	0·540	0·537
Chromium, per cent.	1·17	1·18	1·18

The presence of tungsten or molybdenum would vitiate the result.

Methods in which methylene blue is used have the advantage that this reagent may be used quantitatively in presence of hydrochloric as well as sulphuric acid. Moreover, owing to the excellent character of the end-point with titanous chloride in warm solutions, very small quantities of substance may be rapidly and accurately estimated by suitable adjustment of the strength of the titanous choride and methylene blue solutions used.

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