

# Use of Vanadous Sulphate as a Reducing Agent.

## Part I.

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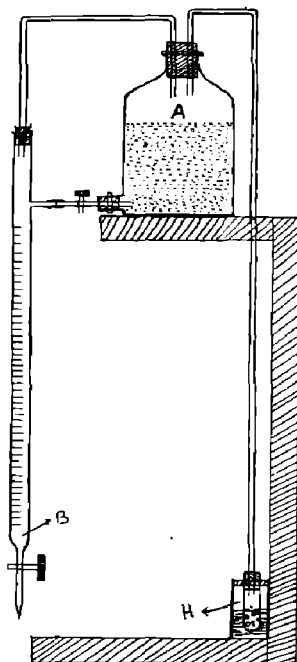
It seems that no systematic study has been made on the reducing property of vanadous salts. Though it has been stated by Piccini, and others (Piccini, *Z. anorg. Chem.*, 1899, 19, 204; Piccini and Marino, *ibid.*, 1902, 32, 55; Marino, *ibid.*, 1906, 50, 49; Rutter, *ibid.*, 1907, 52, 368) that salts of copper, silver, tin, gold, platinum and mercury are reduced to the metal by the vanadous salts; but these investigations are more or less qualitative. Russel (*J. Chem. Soc.*, 1926, 497) has published a note stating that vanadous sulphate is a more powerful reducing agent than titanous sulphate, reducing with greater ease all the inorganic and organic substances reduced by the latter. Russel, however, did not give any experimental evidence in support of his statement. Konrad and Masse (*Z. anal. Chem.*, 1934, 97, 241) have recently published a paper on the use of divalent vanadium salt as a reducing agent in potentiometric analysis. The object of the present investigation is to make a quantitative study on the reducing action of vanadous sulphate upon various inorganic and organic substances and to see whether it can be used as an analytical reagent in volumetric analysis.

### EXPERIMENTAL.

*Preparation of vanadous sulphate.*—Vanadous sulphate is very easily oxidised by air. Its double salt with ammonium sulphate is however more stable. Hence a solution of vanadous ammonium sulphate  $\text{VSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  was used as the reducing agent. It was prepared by the electrolytic reduction of vanadyl sulphate in presence of ammonium sulphate as follows (*cf.* Muller, "Elektrochemische Practikum," 1920).

*Apparatus.*—The electrolytic vessel consisted of a thick walled cylindrical battery glass jar of 9 cm. height and 7 cm. diameter.

FIG. 1.



A—Aspirator. B—Burette.  
H—Hydrogen generator.

This was closed with a rubber cork through which passed a porous clay cylinder of 12 cm. high and 4.5 cm. in diameter. The anode consisted of a lead foil in the form of a cylinder and was placed into the porous cell. Surrounding the clay cylinder was the cathode consisting of a lead cylinder of 4 cm. high. *Catholyte* consisted of a solution of vanadyl sulphate in sulphuric acid containing some ammonium sulphate and *anolyte* consisted of 1 part of concentrated sulphuric acid mixed with 2 parts of water.

The vanadyl salt was reduced by passing a current of 4 amp. from a series of storage cells having an *e.m.f.* of 30 volts. Carbon dioxide was all along passed during electrolysis. Reduction was complete in course of 2-3 hours when the colour of the solution gradually changed from blue to green and finally to violet or lavender. The solution from the electrolytic vessel was then transferred into a storage bottle which had been previously freed from air by passing a current

of carbon dioxide. The solution was diluted with air-free cold water and sufficient sulphuric acid so that it was about 2N with respect to sulphuric acid and 0.1N with respect to ferric salt. The solution was preserved in an atmosphere of hydrogen. An arrangement of the apparatus for using the reagent is shown in Fig. 1.

#### *Some Qualitative Reactions of Vanadous Sulphate.*

The reducing action of vanadous salts is in the great majority of cases, far more energetic than that of other acid reducing agents. With strong nitric acid it reacts violently with evolution of nitrous fumes. Potassium nitrate in presence of hydrochloric acid is reduced

with the formation of nitric oxide. Chlorates are reduced to chlorides. Salts of persulphuric acid are reduced to sulphates. Sulphurous acid is instantaneously reduced to hydrosulphurous acid with the formation of sulphuretted hydrogen and free sulphur. Ferric salts are reduced to ferrous salts. Ceric salts are reduced to cerous state.

Among organic substances nitro compounds (*e.g.*, nitrobenzene, nitrotoluene, picric acid, etc.) are reduced to corresponding amino compounds. Aldehydes and ketones are reduced to corresponding alcohols (*cf.* Connaut and Cutter, *J. Amer. Chem. Soc.*, 1926, **48**, 1019).

Among organic dyes, indigo, methylene blue, safranine, congo red, malachite green, auramine primuline and practically all the dyestuffs which are capable of yielding *leuco* compounds are reduced by the reagent. In most of these cases, as will be shown later on, the reduction is quantitative.

#### *Application of the Vanadous salt in Quantitative Analysis.*

The solution was first of all standardised. For this purpose 25 c.c. of a standard solution (0.1N) of ferrous ammonium sulphate were carefully oxidised with potassium permanganate of about  $N/50$  strength until a faint pink colouration was obtained. A large excess of potassium sulphocyanide was then added and the ferric iron titrated with the vanadous sulphate in an atmosphere of carbon dioxide until the red colouration due to ferric sulphocyanide entirely disappeared. In order to avoid the necessity of oxidising ferrous ammonium sulphate with permanganate for every standardisation, a large volume (about 2 litres) of a standard iron alum solution was prepared. The iron alum solution which retained the same strength for indefinite period was used in all subsequent cases for standardising the vanadous sulphate solution.

#### *Estimation of Iron.*

Solutions of ferric iron may be titrated directly with vanadous sulphate solution, using an excess of potassium sulphocyanide as inside indicator. It is immaterial whether the iron is present in sulphuric or hydrochloric acid solution, but the presence of some mineral acid is essential, because the sulphocyanide indicator is otherwise not sensitive. For the estimation of ferrous iron it must be first oxidised to the ferric state and then titrated.

*Estimation of iron in iron wire.*—Merck's G. R. steel wire (1.4 g.) was dissolved in sulphuric acid and the solution was made up to 250 c. c. A known volume of this solution was just oxidised with potassium permanganate and then titrated with the vanadous salt.

TABLE I.

Strength of vanadous soln. =  $0.7776N/10$ . 1 C. c. = 0.004354 g. Fe.

	Vol. of iron soln.	Vol. of vanadous salt reqd.	Amount of iron in the wire.
1.	25 c. c.	32.05 c. c.	99.7 %
2.	25	32.0	99.5
3.	20	25.65	99.5
4.	30	38.50	99.8

*Estimation of iron in hæmatite.*—Finely powdered sample of the ore (2 g.) was dissolved in hydrochloric acid and the solution made up to 250 c. c. 25 C. c. of this solution were treated with ammonia and hydrogen peroxide, boiled, acidified strongly with sulphuric acid and then titrated with vanadous sulphate using sulphocyanide as an indicator.

TABLE II.

Strength of vanadous soln. =  $1.48N/10$ . 1 C. c. = 0.008288 g. Fe.

	Vol. of iron soln.	Vol. of vanadous soln.	Amount of iron found.	Found by dichromate method.
1.	25 c. c.	15.2 c. c.	62.98%	
2.	25	15.15	62.80	62.90%
3.	25	15.15	62.80	

#### *Estimation of Copper.*

A known volume of a standard solution of copper sulphate was mixed with a known amount of the standard ferric alum solution and an excess of potassium sulphocyanide. The mixture was titrated with the vanadous sulphate when the copper was first precipitated as white

cuprous sulphocyanide and then the red ferric sulphocyanide was reduced to colourless ferrous salt which remained in solution. The amount of potassium sulphocyanide must be in excess, and as long as this was the case varying amounts of this reagent did not affect the results. By subtracting the volume of the vanadous salt required for the known amount of iron from the total volume, the amount of vanadous salt used for reducing copper was found out.

Experiment, however, having shown that cupric salts are readily reduced by ferrous salts in acid solution and that the amount of vanadous sulphate used in a copper estimation was the same with or without the addition of pure ferrous salt, the mode of titration was simplified by adding some pure ferrous sulphate (free from ferric iron) and potassium sulphocyanide to the copper solution and titrating direct with the vanadous sulphate.

TABLE III.

Strenght of vanadous sulphate =  $0.776N/10$ . 1 C. c. =  $0.004898g$ . Cu.

Vol of Cu <sup>++</sup> soln.	Vol of V <sup>++</sup> soln.	Amount of Cu found.	Remarks.
10 c.c.	7.3 c.c.	100.06%	Titrations carried out in presence of 1c. c. of pure ferrous ammonium sulphate soln.
10	7.3	100.06	
20	14.6	100.06	
10	13.4	100.06	Titrations made after the addition of 5c. c. of ferric alum soln. 5C.c. ferric alum soln. = 6.1c.c V <sup>++</sup> soln.
10	13.4	100.06	
20	20.7c.c.	100.06	

Copper was also estimated from the solution by electrolytic and iodometric methods ; the former method gave 100.3% Cu and the latter 99.93% Cu.

#### *Estimation of Chromium.*

For the determination of chromium the chromic salts must be converted into chromic acid. This was effected by oxidising the chromic salt with sodium peroxide, boiling off the excess of oxygen

and then neutralising with sulphuric acid. After cooling the solution in a conical flask, an excess of vanadous sulphate was run into the mixture. The excess of vanadous salt was then titrated back with the standard ferric alum solution using potassium sulphocyanide as an indicator. It is necessary to note here that potassium sulphocyanide should not be added until all the chromic acid has been reduced, because chromic acid acts upon ferric sulphocyanide producing persulphocyanogen. (cf. Knecht and Hibbert, "Volumetric Analysis".)

Pure potassium dichromate (2.4895 g.) was dissolved in water and the solution was made up to 500 c. c. A known volume of this solution was reduced with an excess of vanadous sulphate which was then titrated back with the standard ferric alum solution.

TABLE IV.

Vanadous sulphate soln. = 1.42N/10. Ferric alum soln. = 0.9472N/10

Vol of dichromate soln.	Vol. of vanadous soln.	Vol of Fe <sup>+++</sup> soln.	Amount of chromium Found. Present.	
10 c.c.	10 c.c.	4.85c.c.	0.01769g.	
10	10	4.90	0.01761	0.01760g.
10	10	4.90	0.01761	

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