

however, seem to be purely accidental. Furthermore, the three series yield average results in practical unanimity.

In the following table the final average of this research is compared with that of Baxter and Jones with silver phosphate:

	Ag=107.88.	Ag=107.87.	Ag=107.86.
PBr ₃	31.027	31.024	31.021
Ag ₃ PO ₄	31.04	31.03	31.02

Summary of Results.

1. A method is described for the preparation of pure phosphorus tribromide.

2. It is shown that the precipitation of the halogen of phosphorus halides after decomposition with water, can safely be done only after the oxidation of the greater portion of the phosphorous acid produced.

3. A method is described for the determination of the bromine in phosphorus tribromide by comparison with silver and as silver bromide.

4. The molecular weight of phosphorus tribromide referred to silver 107.88 is found to be 270.775, whence phosphorus has the atomic weight 31.027. If silver is taken at 107.87, the atomic weight of phosphorus becomes 31.024. These values agree very closely with those found by the analysis of silver phosphate by Baxter and Jones.

An attempt to prepare and analyze phosphorus trichloride in a similar manner is now under way in this laboratory.

We are particularly indebted to the Carnegie Institution of Washington for generous pecuniary assistance in carrying out this investigation.

CAMBRIDGE, MASS.

THE REDUCTION OF VANADIC ACID IN CONCENTRATED SULFURIC ACID SOLUTION BY HYDROGEN PEROXIDE AND BY PERSULFATES.

BY J. R. CAIN AND J. C. HOSTETTER.

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Gregory¹ recently described a colorimetric method for vanadium depending on the colors developed when concentrated sulfuric acid solutions of vanadium and strychnine are mixed. It seemed likely from his statements and from others in the literature that the strychnine colors develop only with pentavalent vanadium. We satisfied ourselves that quadrivalent vanadium compounds, at least, give no colors. However, concentrated sulfuric acid solutions of vanadium containing small amounts of the latter are very apt, from various causes, to become reduced to quadrivalent vanadium when carrying out Gregory's method, and as we desired to avoid the use of potassium chlorate, as recommended by him, we tested various oxidizing agents. Among others, hydrogen peroxide

¹ *Chem. News*, 100, 221 (1909).

was used. . But, judging from the colors developed by treating with hydrogen peroxide and adding strychnine, the peroxide treatment was unsuccessful. This seemed so surprising that stronger solutions of vanadium peroxide in concentrated sulfuric acid were tested as to their behavior with hydrogen peroxide. To our surprise we found that vanadium pentoxide in such solutions was immediately and quantitatively reduced to the quadrivalent condition by the peroxide. This was shown on the one hand by the sudden color change from the orange or straw-color of sulfuric acid solutions of the pentoxide to the deep blue of the quadrivalent vanadium compounds, and on the other hand by titration against permanganate. Indeed, this affords a very convenient method for standardizing pure vanadium solutions. All that is necessary is to evaporate the solution with concentrated sulfuric acid until fumes are given off freely, cool, add a slight excess of 3% hydrogen peroxide, cover the flask and fume strongly for a few minutes more to destroy the excess of peroxide, after which the solution may be titrated against permanganate. We made some tests showing that molybdenum and titanium are not similarly reduced by hydrogen peroxide; also iron is not reduced.

Peroxides of zinc, barium, magnesium and sodium behaved in the same manner as hydrogen peroxide; however, the reduction succeeds best with the latter. Barium peroxide, particularly, should not be used where one is standardizing vanadium solutions, inasmuch as the resulting precipitate carries vanadium which would escape titration.

It was also found that concentrated sulfuric acid solutions of vanadium pentoxide could be reduced with persulfates. Our experiments were carried out with potassium and ammonium persulfates. Inasmuch as it is known that persulfates in concentrated sulfuric acid change more or less rapidly to Caro's acid, and since Caro's acid is sometimes made by adding hydrogen peroxide to concentrated sulfuric acid, it seemed quite likely that Caro's acid caused, or took part in, the reaction. Accordingly, a quantity of this reagent was prepared¹ by slowly dropping perhydrol into sulfuric acid (50% by volume) cooled by a freezing mixture. After allowing ten minutes for the system to reach a condition of equilibrium, the excess of peroxide was destroyed by permanganate. Now, on adding the reagent thus prepared to a concentrated sulfuric acid solution of vanadium pentoxide, the reduction took place, as expected, so there seems but little doubt that the reaction is really between Caro's acid and vanadium pentoxide. We have not investigated the mechanism of the reaction, but it seems quite possible that such an investigation would throw some light on the still rather obscure question as to the constitution of Caro's acid.

We have found no references in the literature, in hand-books nor in

¹ Baeyer and Villiger, *Ber.*, 34, 853 (1901).

text-books on quantitative analysis, to this reaction, and believe the observation to be new. It is of interest, perhaps, to note certain observations which show that some investigators have probably had this phenomenon accompanying others, without, however, fully recognizing or explaining it. Thus, Scheuer¹ analyzed barium and other pervanadates by treating them in a flask with dilute sulfuric acid, boiling until no more oxygen was given off, and measuring the amount of oxygen evolved. Hydrogen peroxide is liberated under these conditions and if the concentration of sulfuric acid is right, some or all of the vanadium may be reduced to the quadrivalent condition. Speaking of the analysis of barium pervanadate, Scheuer says, concerning the operation of boiling the solution to expel oxygen: "Dies ist beendet wenn die anfangs rote Lösung (primary action of peroxide on vanadium, giving pervanadic acid) eine hellgrüne Färbung angenommen hat." The "hellgrüne" color must have been that of a mixture of V_2O_4 and of V_2O_5 , due to a partial reduction of the V_2O_5 by hydrogen peroxide. However, Scheuer says "In die Filtrate fand sich noch die freie Vanadinsäure. . . .," and then gives instructions for determining it by reducing with sulfur dioxide and titrating against permanganate. Also, Cammerer,² in preparing pervanadic acid by causing hydrogen peroxide to react with solid vanadium pentoxide, found that the aqueous solution of the reaction product, when evaporated on the steam-bath, deposited a greenish colored substance giving, in dilute sulfuric acid, a green solution which reduced permanganate. More recently, Trautmann,³ in analyzing ferrovanadium, fuses it with sodium peroxide, extracts the fusion with water and filters. The solution, which contains the vanadium and an excess of hydrogen peroxide, is acidified with sulfuric acid, and Trautmann states that at this stage he often observed a reduction, after boiling off the hydrogen peroxide. It seems very likely that here, also, conditions are sometimes right for reduction of vanadic acid by hydrogen peroxide.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NEW HAMPSHIRE COLLEGE.]

NEW COMPOUNDS OF SAMARIUM AND NEODYMIUM.

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The following compounds were prepared during a search for salts of the rare earths that might be useful for fractionating:

Samarium Ethylsulfonate $(C_2H_5SO_3)_6Sm_2 \cdot 6H_2O$.—Ethylsulfonic acid was heated nearly to boiling and small quantities of samarium oxide added

¹ *Z. anorg. Chem.*, **16**, 289 (1898).

² *Chem. Ztg.*, **15**, 958 (1891).

³ *Z. anal. Chem.*, **50**, 371 (1911).