the influence of alkaline nitrates upon the polarization of sugar solutions. The tests were executed with both aqueous and alcoholic solutions, and both in the presence and absence of lead subacetate.

In aqueous solution the influence of potassium and sodium nitrates was almost inappreciable, but in alcoholic solutions, in the presence of lead subacetate, there was quite a considerable diminution in the polariscopic readings.

The author concludes that it is inadvisable to employ alcohol as a solvent in polariscopic work, especially where lead subacetate is used.

[TO BE CONTINUED.]

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE ROSE POLYTECHNIC INSTITUTE.]

THE VOLUMETRIC DETERMINATION OF PHOSPHORUS IN STEEL.[1]

BY W. A. NOYES AND E. D. FROHMAN.

Received June 18, 1894.

VERY full directions for the volumetric determination of phosphorus in steel have been recently given by C. B. Dudley and F. N. Pease.[2] The method is rapid and easy of execution and gives concordant results in the hands of careful workers. There is, however, an uncertainty of about ten per cent. as regards the factor which should be used for converting the iron equivalent of the permanganate solution into the phosphorus equivalent. The most careful determination of the character of the products obtained by reducing molybdic anhydride with zinc and sulphuric acid seems to be that of v. der Pfordten,[3] who finds that when solutions are reduced and titrated with but slight exposure to the air the molybdenum is reduced to a form corresponding to the oxide Mo_2O_3. If this is true one molecule of molybdic anhydride requires, after reduction, the same amount of oxygen for oxidation as three atoms of iron. If we assume, further, that the yellow precipitate contains twelve molecules of molybdic anhydride for one atom of phosphorus, it follows that

---

[1] The work here described was presented to the Faculty of the Rose Polytechnic Institute for the degree of Bachelor of Science by E. D. Frohman.

[2] *J. Anal. Appl. Chem.*, 7, 108. This JOURNAL, 15, 519.

[3] *Ann. Chem.*, (Liebig) 222, 155.

one atom of phosphorus is equivalent to thirty-six atoms of iron. The iron equivalent of the solution should, therefore, be multiplied by $\frac{31}{36 \times 56}$, or by 0.01538, to find the phosphorus equivalent.

Werncke,[1] however, claims that the molybdenum is reduced to a form corresponding to the oxide $Mo_{12}O_{19}$. This would give the factor 0.01628.

Blair[2] follows Werncke and gives factors which reduce to the one last given.

Dudley and Pease[3] assume the same ratio between molybdic anhydride and iron but a different and empirical ratio between phosphorus and molybdic anhydride. Their factors combined give the factor 0.01724.

Doolittle and Eavenson[4] give factors which, when reduced to the same form, give the factor 0.0160.

These facts led us to take up a study of the question in order to determine,, if possible, the cause of the differences and what the true factor is.

We undertook first the determination of the form to which the molybdenum is reduced. For this purpose we intended to use known amounts of pure molybdic anhydride. On examining the molybdic anhydride on hand, which had been bought as chemically pure, we found that it contained considerable quantities of ammonia and also some sodium. On account of the difficulty of preparing the anhydride in pure condition we determined next to use sodium molybdate. This was prepared from the anhydride by dissolving in the calculated amount of sodium hydroxide and crystallizing the salt obtained from water. When dried over sulphuric acid *in vacuo* the salt contains two molecules of water of crystallization. This is completely expelled at 250°

0.5713 gram of the salt lost 0.0823 gram H_2O at 250°.

0.1710 gram of the salt lost 0.0249 gram H_2O at 250°.

Calculated for $Na_2MoO_4+2H_2O$:		Found.	
		I.	II.
$2H_2O$	14.88	14.40	14.56

---

[1] *Ztschr. anal. Chem.*, 14, 9.

[2] "Chemical Analysis of Iron," first edition, p. 86.

[3] This JOURNAL, 16, 230.

[4] Ibid. 16, 243.

The purity of the dry salt was further established by determining the amount of sodium in it by gentle ignition in dry hydrochloric acid as described by E. F. Smith and Philip Maas.[1]

0.3620 gram of the dry salt gave 0.2044 gram NaCl.

0.1148 gram of the salt gave 0.0648 gram NaCl.

Calculated for Na_2MoO_4.		Found. I.	Found. II.
NaCl	56.70	56.46	56.44.

For reduction 4.3405 grams of this sodium molybdate, dried at 250°, were dissolved in 200 cc. of water. Ten cc. of the solution, therefore, contained 0.1517 gram of molybdic anhydride.

The permanganate solution used was standardized by means of ammonium oxalate and of ferrous ammonium sulphate.

0.8923 gram of the ferrous ammonium sulphate required 17.88 cc. of the solution.

0.2077 gram of the ammonium oxalate required 22.93 cc. of the solution.

These results give respectively 0.007129 and 0.007144 as the iron equivalent of the solution, and one cc. of the solution contains 0.00102 gram of available oxygen.

For reduction ten cc. of the solution of sodium molybdate referred to above were diluted with 140 cc. of water and fifty cc. of dilute sulphuric acid (1 : 5 by vol.), and the solution was passed through the "reductor"[2] and followed by 100 cc. of dilute sulphuric acid (1 : 100) for washing. The solution was then titrated in the flask. In all the experiments a correction was made for the amount of potassium permanganate required in blank experiments with the same quantities of dilute sulphuric acid. The corrected values are given throughout this paper.

In the first experiments amounts of potassium permanganate were required which corresponded to from 15.90 to 16.35 per cent. of oxygen as compared with the amount of molybdic anhydride present. If reduced to the form corresponding to the oxide Mo_2O_3 16.67 per cent. of oxygen should be required, while for the form $Mo_{12}O_{19}$ but 15.74 per cent. is required. The results were not concordant and a little study of the matter led to the discovery that the reduced solution is very easily reoxidized by

---

[1] This JOURNAL, 15. 398.

[2] *J. Anal. Chem.*, 3, 123.

exposure to the air or by oxygen contained in water used for dilution. We have since found that Werncke states this fact very clearly in his paper,[1] but his statement seems to have been overlooked by recent workers and curiously enough Blair states almost exactly the contrary.

The following illustrations of the ease with which the solution is oxidized may be given. A solution reduced as usual and which would have required at least sixteen per cent. of oxygen for its oxidation was poured into a beaker and back into the flask several times and then required only 14.89 per cent. of oxygen. A second solution reduced and then poured back and forth six times required only 13.74 per cent. of oxygen.

As it is evident from these experiments that the reduced solution must be titrated with very little exposure to the air, the reduction was next effected as follows: ten cc. of the sodium molybdate solution were diluted with 140 cc. of water and fifty cc. of dilute sulphuric acid. In the flask which was to receive the solution were placed two grams of acid sodium carbonate and five cc. of dilute sulphuric acid, thus expelling the air almost completely. A small amount of very dilute sulphuric acid was passed through the reductor first, then the molybdate solution as described and then 100 cc. of water containing five cc. of dilute sulphuric acid for washing. During all, care was taken to keep the reductor full and allow no air to pass through it. The reduced solution was titrated immediately *in the reductor flask*. Two solutions reduced in this way required respectively 24.8 cc. and 24.83 cc. of the permanganate solution, or 16.74 per cent. and 16.76 per cent. of oxygen.

The use of acid sodium carbonate for ordinary work would be somewhat troublesome and we next tried the effect of expelling most of the air from the reductor flask by passing through the reductor sixty cc. of dilute sulphuric acid (1 : 30) and following this with the solution to be reduced and the acid wash-water, taking care throughout that no air entered through the reductor tube. Ten cc. of the solution of sodium molybdate diluted with 140 cc. of water and fifty cc. of diluted sulphuric acid (1 : 5),

---

[1] *Ztschr. anal. Chem.*, **14**, 7.

[2] "Chemical Analysis of Iron," p. 89.

required, when reduced in this way, 24.81 cc. of the permanganate solution, or 16.74 per cent. of oxygen.

Experiments were next tried with pure crystals of ordinary ammonium molybdate. This has the composition $(NH_4)_6Mo_7O_{24}+4H_2O$, and should require if the molybdenum is reduced to the form corresponding to the oxide Mo_2O_3, 13.59 per cent. of oxygen for reoxidation; 0.2037 gram of the salt required, after reduction as last described, 27.48 cc. of the permanganate solution; 0.2025 gram of the salt required 27.32 cc. These amounts correspond to 13.76 and 13.76 per cent. of oxygen.

Some molybdic anhydride was next prepared by gently igniting in a porcelain dish a comparatively pure specimen until all ammonia was expelled and the substance had changed to a pure yellow color, 0.1722 gram of this anhydride required, after reduction as last described, 27.76 cc. of the permanganate solution and 0.1726 gram required, 28.23 cc. or 16.44 and 16.68 per cent. of oxygen.

These experiments prove conclusively that if the reduction is properly executed the molybdenum is reduced to the form corresponding to the oxide Mo_2O_3. The conditions are that the solution should be preceded by some dilute sulphuric acid so that most of the air in the reductor flask may be expelled before the reduced solution enters it, that the sufficiently dilute solution shall pass the reductor slowly[1] and be followed by the acid wash-water without allowing air to enter the reductor at the top, and that the reduced solution shall be titrated at once and *without further dilution*. The reduced solution should be of a pure green color and not olive-green.

After establishing the ratio between molybdic anhydride and iron for the permanganate solution there still remain two questions before we can consider the ratio between the iron and phosphorus as settled.[2] These are, what is the ratio between molybdic anhydride and phosphorus in the yellow precipitate, and is the precipitation of the phosphorus practically complete in the case of the small amounts usually present in a steel analysis?

---

[1] See Doolittle and Eavenson. This JOURNAL, 16, 241.

[2] The paper of Prof. S. W. Johnson (this JOURNAL, 16, 462) has appeared since this was written. The presence of aluminum or manganese in its precipitate would not affect the results of the volumetric method. Iron, if present, would affect the results and that point deserves a more careful study.

The fact that there are twelve molecules of molybdic anhydride for one atom of phosphorus has been so thoroughly established by different observers that it seems scarcely necessary to discuss the matter or even to cite authorities. The experiments of Dudley and Pease[1] can not be considered as having much bearing on this question when we consider the extreme difficulty of the gravimetric determination of such minute amounts of phosphorus and the facts with regard to the reduction of the molybdenum which have been considered above.

The question as to the completeness of the precipitation is more difficult but we believe it is best studied by the precipitation of solutions containing known amounts of phosphorus under conditions practically identical with those of the steel analysis.

A solution of sodium phosphate was prepared of such strength that one cc. contained 0.000102 gram phosphorus (determined by evaporating a measured volume of the solution, igniting and weïghing the sodium pyrophosphate), three cc. of this solution were placed in a flask with five grams of ferrous sulphate, free from phosphorus (equivalent to about one gram of iron), nitric acid was added, then potassium permanganate, and the precipitation of the phosphorus was effected exactly as directed by Dudley and Pease. The precipitate, after washing, was dissolved and reduced as described in the first part of our paper. In duplicate experiments 3.08 and 3.0 cc. of permanganate were required, which gives 0.34 and 0.33 mgm. of phosphorus instead of 0.31 mgm. actually present, if we use the theoretical factor which we have deduced for the relation between iron and phosphorus. Dudley's factor on the other hand would give 0.37 and 0.38 mgm.

Determinations were also made of the phosphorus in three samples of steel containing known amounts of phosphorus which were kindly furnished us by Dr. Dudley. They are the same steels to which Dr. Dudley has already referred. We give the results of our analyses calculated by the theoretical factor obtained by multiplying the iron equivalent of the permanganate solution by 0.01538, and also by the empirical factor of Dudley and Pease.

---

[1] This JOURNAL, 16, 229.

	Gravity determination, Per cent.	Volumetric determination. By theoretical factor.	By factor of Dudley and Pease.
Steel No. 1	0.040	0.040	0.045
“ “	....	0.040	0.045
“ “	....	0.039	0.044
Steel No. 2	0.053	0.050	0.056
“ “	....	0.052	0.058
Steel No. 3	0.032	0.029	0.032
“ “	....	0.034	0.038
“ “	....	0.032	0.036

It is evident that the theoretical factor gives results which agree closely with the gravimetric determinations while the results calculated by the empirical factor of Dudley and Pease are decidedly too high. The evidence that the precipitation of the phosphorus is practically complete is quite satisfactory. It will be remembered that steel No. 2 contains arsenic. Our results seem to indicate that the arsenic is not precipitated to an appreciable extent with the phosphorus.

If the theoretical factor for the ratio between the iron and phosphorous equivalents of a potassium permanganate solution shall be confirmed by other observers, as we feel confident that it will be, the volumetric determination will be placed on so firm a basis that, at least in the absence of arsenic, the results obtained by it must be considered as more reliable than those obtained by any gravimetric method now in use. This cannot be true so long as the determination depends on an empirical factor, for any empirical factor is likely to vary with the amounts of phosphorus present and would not be applicable to steels containing widely different amounts of phosphorus.

TERRE HAUTE, June 15, 1894.

THE ANALYSIS OF MALT.

BY TOM CROSSMAN.

Received June 18, 1894.

IN the JOURNAL for May, 1894, there is an article on the analysis of malt by Dr. Miller. As a few of Dr. Miller's statements are totally opposed by those who have given the chemistry of malt their life study, I feel justified in bringing before your readers the methods of analysis which are in use for the valuation