[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

THE VOLUMETRIC ESTIMATION OF SMALL AMOUNTS OF PHOSPHORUS, USING A STANDARD SOLUTION OF METHYLENE BLUE

BY WILLIAM M. THORNTON, JR. AND H. L. ELDERDICE, JR.

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Introduction

The first titration involving the use of a standardized solution of methylene blue seems to have been described by Hibbert.[1]

She showed that titanium, after reduction by zinc and hydrochloric acid to a titanous salt, could be accurately titrated with this dye, even in the presence of considerable iron, forming methylene white and a titanic salt. Atack[2] has studied the matter of utilizing methylene blue in analytical chemistry more broadly, and, regarding its merits as a volumetric reagent, has called attention to the following properties: (1) great fastness to light; (2) stability of an acid solution of the dyestuff and its leuco compound; (3) ease of conversion to leuco body by reducing agents, and the converse by oxidizing agents; and (4) high tinctorial power, since it is possible to titrate with a 0.002 N solution. On the other hand, methylene white is sensitive toward atmospheric oxidation, and this is also true of some of the metallic salts in their lower valences; hence it is quite necessary to carry out the titrimetric processes under a protective blanket of an indifferent gas.

In addition to the above, Knecht and Hibbert[3] have succeeded in estimating tungsten, and Knecht and Atack[4] have, in like manner, determined molybdenum with apparently good results. In the latter case, the molybdic acid is reduced by zinc in hydrochloric acid to molybdenum trichloride; thereafter it is oxidized back to molybdenum pentachloride (the highest chloride that molybdenum is known to form) by methylene blue in the sense of the equation, $C_{16}H_{18}N_3SCl + MoCl_3 + 2HCl = C_{16}H_{20}N_3SCl + MoCl_5$. Moreover, the experiments on molybdenum and also those on tungsten confirm Hibbert's observation,[1] namely, that ferrous chloride does not reduce methylene blue.[5]

It seemed, therefore, that the reaction between trivalent molybdenum and methylene blue might well be made the basis of a new process for the estimation of phosphorus in the precipitate of ammonium phosphomolybdate,[6] the form in which it is commonly separated. This would avoid the error accompanying the use of permanganate[7] as an oxidizing agent, due

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[1] Hibbert, *J. Soc. Chem. Ind.*, **28**, 189 (1909).

[2] Atack, (a) *J. Soc. Dyers Colour.*, **29**, 9 (1913); (b) **31**, 183, 203 (1915); (c) *Analyst*, **38**, 99 (1913).

[3] Knecht and Hibbert, *Analyst*, **36**, 96 (1911).

[4] Knecht and Atack, *ibid.*, **36**, 98 (1911).

[5] Atack, Ref. 2b, notes two exceptions to the general rule that ferrous salts do not reduce methylene blue, namely (1) ferrous ammonium sulfate in strong hydrochloric acid and (2) ferrous tartrate, but in neither case is the action quantitative.

[6] Compare Blair and Whitfield, THIS JOURNAL, **17**, 747 (1895). See also Fairbanks, *Am. J. Sci.*, [4] **2**, 181 (1896). Randall, *ibid.*, [4] **24**, 315 (1907).

[7] Blair, "The Chemical Analysis of Iron," 8th ed., J. B. Lippincott Co.. **1918**, p. 87.

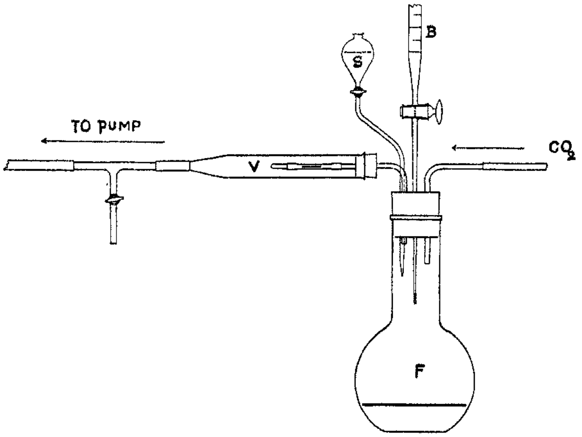
to the iron occluded by the precipitate or derived from the zinc used in the reduction.

Experimental Part

Preliminary experiments at once revealed the fact that, owing to the intensely green color of pentavalent molybdenum, the change from green to greenish blue (methylene blue in hydrochloric acid) at the end-point is extremely difficult to detect except when very small amounts of molybdenum are present. Consequently, in the work to be described, the expedient was adopted of dividing the test solution into aliquot parts so that the amount of phosphorus actually experimented with did not exceed 0.0004 g. (corresponding to 0.015 g. of molybdenum). The result thus obtained was then multiplied by the proper number (usually 5) in order to arrive at the quantity of the desired constituent in the entire sample.

Standard solutions of the dye were prepared by dissolving "medicinal" methylene blue in water, filtering and adding more water until the requisite concentration had been reached, 4 g. to the liter being a suitable strength for most purposes. Standardization was then effected by titrating measured portions, acidified with hydrochloric acid and kept hot, with a known solution of titanous sulfate[8] in an atmosphere of carbon dioxide. The titer of the titanous sulfate solution had been previously established either by means of specially prepared ferrous ammonium sulfate or indirectly with certified sodium oxalate from the Bureau of Standards.

Our first estimations were made on a solution of ammonium molybdate, which had been prepared from recrystallized material and standardized by carefully evaporating measured portions to dryness and igniting to molybdic anhydride.



Apparatus.

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[8] Knecht and Hibbert, "New Reduction Methods in Volumetric Analysis," Longmans, Green and Co., **1918**, pp. 33 and 80. See also Hendrixson and Verbeck, THIS JOURNAL, **44**, 2382 (1922).

The assay was placed in the Johnson sulfur flask F of 275 cc. capacity, which was fitted with a 4-hole rubber stopper containing inlet and outlet tubes, dropping funnel and buret tip. The exit tube was terminated by a Bunsen valve V, and this was enclosed in a larger tube tapering at the forward end and leading eventually to the pump, the intervening T-tube with stopcock being intended to permit relieving the suction without changing the rate of flow of water through the pump. Five g. of 30-mesh zinc having been introduced into the flask, the suction was turned on and continued throughout the reduction; after 2 to 3 minutes had elapsed, carbon dioxide from a Kipp generator (not shown in the figure) was passed through the flask for 10 minutes, thus removing practically all air from within the system. About 50 cc. of hydrochloric acid (d., 1.18) was then admitted from the tap funnel S, *very slowly*, so that the reduction proceeded at a moderate rate and went to completion. As soon as vigorous action had ceased, the solution was boiled to dissolve all remaining zinc, only a few seconds being required, whereupon the titration was accomplished with standard methylene blue already contained in the buret B. The following color changes were observed: salmon-pink to light yellow, light yellow to light green and finally light green to dark green—the last transformation from light to dark green on the further addition of a drop of methylene blue denoting the point of complete reaction.

The results of several experiments carried out in this manner are recorded in Table I.

TABLE I

DETERMINATION OF MOLYBDENUM

0.01469 g. of molybdenum taken

Molybdenum found G.	Molybdenum error G.	Molybdenum found G.	Molybdenum error G.
0.01445	−0.00024	0.01458	−0.00011
0.01451	−0.00018	0.01459	−0.00010

Although these data are sufficient to show that the error in the process is not excessive, still, on attempting to increase the size of the sample to anything like that employed by Knecht and Atack[9] an indeterminate end point was obtained.

The next trials were made with a solution of sodium ammonium phosphate which had been standardized by the simple but accurate method of evaporating measured portions to dryness and igniting to sodium metaphosphate.[10]

Five cc. of this solution, corresponding to about 0.0026 g. of phosphorus, was precipitated with the molybdate reagent, made up according to Blair,[11] and the ammonium phosphomolybdate was collected on a filter and washed with acid ammonium chloride solution.[12] The precipitate was then dissolved in ammonium hydroxide (d., 0.973) and the solution was made up to exactly 50 cc. Aliquot parts of 10 cc. were then taken and each was treated as outlined above.

The results appear in Table II.

[9] Ref. 4, p. 100.

[10] Cf. Gooch, *Proc. Am. Acad. Arts Sci.*, **15**, 53 (1879).

[11] Ref. 7, p. 92.

[12] To 1 liter of water 15 cc. of ammonium hydroxide (d., 0.90) and 75 cc. of hydrochloric acid (d., 1.18) were added.

TABLE II

DETERMINATION OF PHOSPHORUS

10/50 Taken as aliquot portion

Phosphorus taken G.	Phosphorus found × 5 G.	Phosphorus found Av. G.	Phosphorus error Av. G.
0.002627	0.002602	0.002606	−0.000021
	0.002602		
	0.002615		
0.002627	0.002625	0.002623	−0.000004
	0.002621		

To test the availability of the method for the determination of phosphorus in steels, "standard samples" from the Bureau of Standards were analyzed. These samples were treated exactly as directed by Blair.[13]

In case aliquot parts were to be taken, the entire ammoniacal solution of the yellow precipitate was transferred to a 50cc. volumetric flask and the solution made up to the mark with water; otherwise, the filtrate and washings were caught directly in the Johnson flask. In dealing with low-phosphorus steel, wherein the division of the test solution proved unnecessary, it was found desirable to increase somewhat the amounts of zinc and hydrochloric acid to insure a complete reduction in the greater volume; accordingly, about 7 g. of the former and 65 cc. of the latter were used. Ordinarily, however, several 10cc. portions were taken; and, from this point on, the procedure followed was exactly like that described above. Table III sets forth the results obtained on 3 different kinds of steel.

TABLE III

ANALYSES OF STEELS

1.0 g. of Basic open hearth steel, B. of S. No. 16a

Aliquot part	Phosphorus found %	Bur. Standards Av. %	Difference %
...	0.034	0.035	−0.001
...	0.034	0.035	−0.001
...	0.035	0.035	0.000
...	0.035	0.035	0.000
...	0.035	0.035	0.000
1.0 g. of Bessemer steel, B. of S. No. 8b			
10/50	0.104	0.104	0.000
10/50	0.104		
10/50	0.104		
10/50	0.104		
2.0 g. of Nickel steel, B. of S. No. 33			
10/50	0.025	0.026	−0.001
10/50	0.025		
10/50	0.026		
10/50	0.026	0.026	0.000
10/50	0.026		

In addition to the above, the phosphoric acid was determined in an argillaceous limestone B. of S. sample No. 1, the preliminary treatment

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[13] Ref. 7, p. 92.

being essentially that of Hillebrand.[14] Except for omitting the permanganate oxidation, the process was completed just as in the case of steels.[15] One g. was taken, 2 aliquot portions of 10/50 used, and 0.183, 0.183% of phosphoric anhydride found as compared with 0.18, the Bureau of Standards average; the difference is +0.003%.

Attempts to estimate the phosphorus in an iron, containing 0.429% of phosphorus, namely Iron D of the Bureau of Standards (Standard sample No. 6c), gave on the average a value nearly 0.02% below the standard figure, showing that, at least in its present form, this is about the upper limit of the method's capacity, since the discrepancies noted are too great for high grade work.[16]

Discussion of the Results

A glance at the results, obviously satisfactory for the quantities of phosphorus involved, will convince one that the absolute error incurred is extremely small, since in the majority of instances it does not appear until the sixth decimal place has been reached. On the other hand, the inconvenience of having to work with such small amounts of material must not be overlooked. This objection reaches its maximum when dealing with materials of unknown phosphorus content, necessitating, of course, a tentative experiment for determining the approximate content before the present method can be intelligently applied. It has seemed to us that the size of the sample might be considerably increased and a definite end-point obtained by some other means of observation. Electrometric titration is suggested, and indeed some experiments have already been made in this direction. Although it will be impossible to complete this work for some time, we wish to reserve the privilege of continuing it.

Interfering Substances

The influence of those substances which are known to vitiate the phosphorus values in other methods of analysis, such as arsenic, vanadium, titanium, etc., has not yet been studied. Some of the steels analyzed were known to contain one or more of these constituents in small amount, and no harmful effect is apparent, but it is reasonable to suppose that they might interfere if present in considerable quantity.[17] The non-interference of iron has already been remarked upon.

Summary

An oxidimetric process for the estimation of small amounts of phosphorus has been satisfactorily worked out, which depends upon the forma-

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[14] Hillebrand, U. S. Geol. Survey, *Bull.*, **700**, 263 (1919).

[15] Analysis by Dorothy Getz.

[16] The graphitic residue, which may contain a trace of phosphorus [Bur. Standards, *Circ.*, **14**, 9 (1916)] was filtered off and rejected; but it is very improbable that any possible loss here could account for the entire error.

[17] Cf. Lundell and Hoffman, *Ind. Eng. Chem.*, **15**, 44 (1923).

tion of the ammonium phosphomolybdate precipitate, solution of this in ammonium hydroxide, reduction to molybdenum trichloride by hydrochloric acid and zinc in an air-free atmosphere and titration to molybdenum pentachloride with a standard solution of methylene blue, on the assumption that the ammonium phosphomolybdate has the normal composition, $(NH_4)_3PO_4.12MoO_3 + nH_2O$.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA]

THE DISSOCIATION OF MOLECULAR HYDROGEN, FROM THE ENTROPIES OF DIATOMIC AND MONATOMIC HYDROGEN

BY GRAHAM EDGAR

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The extent of dissociation of the hydrogen molecule into atoms at high temperatures, and the heat of dissociation, are quantities of considerable interest, particularly from their bearing on the Bohr theory of the structure of the hydrogen molecule.

Langmuir, as the result of deductions from the behavior of hydrogen surrounding a heated tungsten filament, calculated[1] somewhat indirectly the heat of dissociation to be —136,000 cal. at 3000° K. at constant pressure, and the extent of dissociation to be about 2% at the same temperature and atmospheric pressure. Later,[2] as the result of a more extended study, he estimated —90,000 cal. as the heat of dissociation at 3000° K. and constant pressure, and the extent of dissociation to be 1.6% at atmospheric pressure and the same temperature.

The value of —90,000 cal. for the heat of dissociation at constant pressure (—84,000 at constant volume) seems to be rather generally accepted, and is in very good agreement with calculations made from the ionizing potential.[3]

Saha,[4] making use of a simplified form of the Nernst approximation formula, and using —82,000 cal. as the heat of dissociation, has calculated the degree of dissociation of hydrogen at various temperatures and pressures, obtaining results considerably higher than those estimated by Langmuir. His data have been confirmed by Duffendack,[5] who employed a more exact form of the Nernst formula, and obtained results very near to those of Saha and considerably higher than those of Langmuir. Duffendack also carried out experiments which indicated the presence of a con-

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[1] Langmuir, THIS JOURNAL, **34**, 860 (1912).

[2] Langmuir, *ibid.*, **37**, 417 (1915).

[3] Sommerfeld, "Atombau und Spectral-linien," 3rd ed., **1922.**

[4] Saha, *Phil. Mag.*, **40**, 472 (1920).

[5] Duffendack, *Science*, **55**, 210 (1922); *Phys. Rev.*, **20**, 665 (1922).