

let was plugged. As further proof, comparisons were made of the flash point of an oil obtained in the usual way and of the flash obtained by placing a quantity of low flash oil in the overflow cup. The results are shown in Table V.

TABLE V

Test	Sample No. 1087 with 5 cc. of Sample No. 1086 (F. P. = 37°) in the overflow cup		Instrument used
	Sample No. 1087	Sample No. 1086	
No. 1.....	45.4	45.4	B. of M. modified Abel-Pensky
No. 2.....	45.3	45.4	
No. 3.....	45.8	45.4	
Average.....	45.5	45.4	

## SUMMARY

The important factors to be considered in the construction and manipulation of an instrument to determine the flash point of an oil may be stated as follows:

- (1) The conditions under which the test vapors are generated should be as like as possible to the conditions found in practice.
- (2) Corrections should be made for variations from the normal barometric pressure.
- (3) The size and dimensions of the cup.
- (4) The size, shape, depth of immersion and exposed part of the thermometer should be definite and in every case the thermometer should be calibrated.
- (5) The oil should never be exposed for any length of time at temperatures greatly higher or lower than the normal temperature.
- (6) The rate of heating on testing should be constant and at a rate of about 1° C. for lamp oils and 3°-5° C. for high flash-point oils.
- (7) The oil should be uniformly stirred during the test.
- (8) The test flame should be of definite size, should be exposed at a fixed distance above the surface of the oil and exposed for a definite length of time.
- (9) All water should be removed from the oil prior to testing.
- (10) In general testing, so far as possible, the effect of the personality of the operators should be eliminated and the manipulation of the tester made entirely mechanical and automatic.

The most accurate tester and the tester that most nearly reproduces actual working conditions should be adopted for official tests. Considering all of the above factors, it is believed that these two testers, the Abel-Pensky and the Pensky-Martens, as modified by the Bureau of Mines, most nearly meet with the desired conditions.

The Bureau of Mines flash testers have been officially adopted by the National Fire Protection Association, the Independent Petroleum Marketers' Association of the United States and are now being considered for adoption by committees on tests of the National Petroleum Association, the American Chemical Society, the American Society for Testing Materials and the International Petroleum Commission.

BUREAU OF MINES  
PITTSBURGH

## THE TITRATION OF CALCIUM AND MAGNESIUM IN THE SAME SOLUTION

By PAUL J. FOX<sup>1</sup>

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Few determinations are more frequently made in chemical laboratories than those of calcium and magnesium, and the writer was led into the following investigation with a view to lessening the labor required for these determinations: The titration of calcium as oxalate with permanganate is, of course, a well known and standard process, and the titration of magnesium as magnesium ammonium arsenate with sodium thiosulfate in acid solution after the addition of potassium iodide has been described by Meade<sup>2</sup> and by G. B. Frankforter and Lillian Cohen.<sup>3</sup>

It has occurred to the writer that it might be possible to combine these processes in one operation by first precipitating the calcium as oxalate, and then in the same solution and without filtering, precipitating the magnesium as magnesium ammonium arsenate, filtering off and washing the combined calcium oxalate and ammonium magnesium arsenate, dissolving in acid, titrating the calcium oxalate with potassium permanganate and then the magnesium ammonium arsenate with sodium thiosulfate after the addition of potassium iodide. As will be shown in the sequel, this combined method is perfectly feasible, the two titrations not interfering with each other.

The titration of calcium as oxalate calls for no remark except to observe that the objection that the calcium sulfate formed prevents complete decomposition of the calcium oxalate is not, in the writer's experience, valid. With moderate skill in manipulation, it is always possible to obtain good results.

In the titration of the arsenate, however, certain irregularities were encountered. For example, following approximately the directions in the paper of Frankforter and Lillian Cohen, when 10 cc. portions of a certain solution of ammonium arsenate were acidified, and made up to 100 cc. so that 100 cc. contained about 15 cc. concentrated sulfuric acid, cooled, 5 grams potassium iodide added, and titrated after standing 5 minutes, 21.21, 21.52, and 20.78 cc. thiosulfate solution were required to decolorize the solution. All the portions were, of course, measured out by the same pipette and measured over the same portion of the burette. The figures given are selected from many and are representative of the magnitude of the variations. They were measured out and titrated at different times, a series titrated at the same time showing less variation. The end point was always certain and definite.

Many experiments were made to find the cause and remedy for the irregularities, but to cite the figures in detail would scarcely be profitable. The advantages of the improvements suggested are more or less self evident. The principal causes of irregularity—assuming of course that the iodide used is free from iodate or other substance capable of setting free iodine

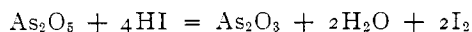
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<sup>2</sup> R. K. Meade, *Jour. Am. Chem. Soc.*, **21**, 146 (1899).

<sup>3</sup> *Jour. Am. Chem. Soc.*, **29**, 1464 (1907).

in acid solution—are (1) the slowness with which pentavalent arsenic sets free iodine in acid solution; (2) in strong solutions, the escape of iodine before titration; (3) especially the effect of light on setting free iodine from hydriodic acid; and (4) the returning color at the end point.

The setting free of iodine from pentavalent arsenic may be represented by the equation



This reaction proceeds from left to right rather slowly. Fine sand was tried as a catalyzer but with no appreciable accelerating effect. Heating to about 40° accelerated the reaction, but the temperature must be so closely managed to avoid a precipitation of yellow arsenic trisulfide, that it cannot be recommended: too many determinations are lost. Removing the reaction products on the right-hand side of the equation naturally suggested itself. It is not practicable to use sulfuric acid of sufficient strength to take up the water, but it was found distinctly advantageous to add the thiosulfate immediately after the potassium iodide, to a light straw color, and then to allow to stand, for 5 to 6 minutes, before titrating to the end point. This procedure also operates to prevent the escape of iodine before titration.

The principal cause of irregularity, however, was found to be light. Of course, titrations were not made in sunlight, but even the diffused daylight of Washington in summer is sufficient to set free considerable iodine. That the light and not the presence of iodates or other oxidizing bodies sets free the iodine was shown by dissolving five grams of the potassium iodide used in recently boiled acidified water, displacing the air in the flask by carbon dioxide, and allowing to stand for some time in the dark. No color was developed.

The returning color at the end point appears to be caused by the incomplete setting free of the iodine by the arsenic and by light. The reaction  $\text{I}_2 + 2\text{Na}_2\text{S}_2\text{O}_3 = 2\text{NaI} + \text{Na}_2\text{S}_4\text{O}_6$  seems to have no tendency, even in the light, to go from right to left.

It was found possible to eliminate the effects of light, or rather to eliminate the irregularities, by placing the Erlenmeyer flask in which the titration was made in the dark during the time it was standing after having had the greater part of the thiosulfate added, and preparatory to completing the titration. Likewise, after bringing to an end point, the flask is allowed to stand in the dark one minute. If there is no return of color the end point has been reached. The darkness was conveniently provided by rolling a hollow cylinder out of black paper and placing it over the flask in which the titration had been made.

In spite of these precautions, however, it is necessary to make a correction for iodine set free otherwise than by arsenate. The correction has the effect of making the variation more nearly uniform. The improvement in results brought about by these precautions is shown by the following experiments: Ten cc. of a solution of ammonium arsenate was diluted to 100 cc. with water containing 15 cc. concentrated sulfuric acid, and 5 grams of potassium iodide added. Sodium thiosulfate (about tenth normal) was added to a light

straw color, and the flask allowed to stand in the dark for about six minutes. The rule was observed to allow eight minutes to elapse between the adding of the potassium iodide and the completing of the titration. Then thiosulfate was slowly added to decolorization, and the flask placed in the black paper cylinder for one minute, and if a color returned, it was discharged. Commonly there was no return of color, if the last drops of thiosulfate had been added slowly. In three experiments, 20.85 cc., 20.82 cc., and 20.80 cc. thiosulfate solution were consumed. In general there was no difficulty in getting check results within one or two drops of tenth normal thiosulfate on titrations of about 20 cc. In this case no correction has been subtracted for light, as the procedure was merely being tested.

The most convenient means of finding the correction for iodine set free by light or by other means than pentavalent arsenic is by titrating with thiosulfate, as described above, two portions of ammonium arsenate solution (of which the exact concentration need not be known) one, say, of 10 cc., and the other of double the amount or 20 cc. If the 10 cc. arsenate required  $x$  cc. thiosulfate solution and the 20 cc. required  $y$  thiosulfate solution, then the correction is  $(2x - y)$  cc. It may be 0.2 to 1.0 cc. Of course the correction may be found by titrating magnesium ammonium arsenate, but it is longer and not necessary. It is not possible to find the correction by making a blank in the ordinary manner, a correction found by such means coming out too low. The following figures show the results of the corrected method of titration of 10 and 20 cc. portions of an ammonium arsenate solution: (The arsenate solution is not the one previously referred to.)

ARSENATE Cc.	THIOSULFATE Cc.	MEAN Cc.
10	20.98	} 20.94
10	20.91	
20	40.83	} 40.92
20	41.02	

From which the correction proves to be  $2 \times 20.94 - 40.92 = 0.96$  cc. This correction is unusually large. In general, it will amount to from 0.3 to 0.7 cc.

A solution of calcium chloride free from magnesium and iron was prepared by boiling a solution of calcium chloride with calcium oxide and acidifying the filtrate barely to acid reaction with hydrochloric acid. A solution of magnesium chloride free from iron and calcium was prepared by boiling magnesium chloride solution with magnesium oxide, filtering, evaporating the filtrate with a little ammonium oxalate, taking up with water and a little ammonia, filtering and slightly acidifying the filtrate. Portions of these were taken for analysis. In the case of the calcium chloride solution it was found gravimetrically, each experiment being in triplicate with unusual care, that 25 cc. yielded 0.1283 gram CaO, 50 cc. 0.2575 gram, 100 cc. 0.5158 gram CaO. Thus if we determine the CaO yield directly on 25 cc. CaCl<sub>2</sub> solution, we find that it amounts to 0.1283 gram. But if we take the difference, 50 cc. — 25 cc. = 0.2575 — 0.1283 gram = 0.1292 gram CaO. So also  $\frac{1}{3}$  (100 — 25) cc. and  $\frac{1}{2}$  (100 — 50) both

equal 0.1292 gram after rounding off the tenth milligrams. Thus 25 cc. of the  $\text{CaCl}_2$  solution is equivalent to 0.1292 gram  $\text{CaO}$ , or 10 cc. = 0.05167  $\text{CaO}$ . In all the experiments the conditions of bulk of solution, temperature, and wash water were kept exactly alike, and the 0.9 mg. difference is evidently owing to the solubility of the calcium oxalate under the conditions of the experiment. This source of error is also mentioned by Hillebrand.<sup>1</sup> Strictly speaking, it is an absolute error which should be applied to each determination, but it will not be necessary to apply it if the permanganate is standardized by weighing out pure Iceland spar, especially if the bulk of permanganate used in standardization does not differ very greatly from that consumed in the analysis. In the case of the magnesium chloride solution, no such solubility error was found. By precipitation with ammonium phosphate, each determination being in duplicate:

10 cc. = 0.0391  $\text{MgO}$

20 cc. = 0.0780  $\text{MgO}$

30 cc. = 0.1173  $\text{MgO}$

Average for 10 cc. = 0.03907  $\text{MgO}$

No volumetric method for magnesium, so far as the author knows, can hope to yield so exact results. It must be remembered, however, that in the present case, the magnesium ammonium phosphate was precipitated under ideal conditions, there being present no other salts, and only slightly more than the calculated amount of ammonium phosphate necessary to precipitate the magnesium. Under working conditions this determination is well known to be subject to a serious plus error.<sup>2</sup> Under working conditions, probably the volumetric method will give as good results as the gravimetric unless special precautions and care are taken with the latter.

For the volumetric solutions the mean of all titrations showed each cc. of permanganate = 0.002816  $\text{CaO}$ . For the thiosulfate each cc. = 0.002074  $\text{MgO}$ .

#### METHOD FOR COMBINED DETERMINATION

The combined determination is made in the following manner: Precipitate the iron and alumina with ammonia or basic acetate in the usual manner.<sup>3</sup> There must always be sufficient ammonium salts present to prevent a precipitation of magnesia when the solution is made *slightly* alkaline. In the filtrate, precipitate the calcium hot with excess of oxalic acid<sup>4</sup> and dilute ammonia added slowly, to slight alkaline reaction, a drop of methyl orange having been added to the solution. Then add sufficient ammonium arsenate to precipitate the magnesia, and slowly add ammonia with constant stirring to the *hot* solution until the magnesium am-

monium arsenate comes down, or if so much calcium oxalate is present that this cannot be observed, add about 10 cc. strong ammonia water. Let cool and add 10 to 15 cc. more strong ammonia. Add the ammonium arsenate to the hot solution within a few minutes after the solution has been made slightly alkaline in the precipitation of calcium oxalate, as magnesium oxalate soon begins to come down, which is, of course, one of the sources of error in the standard gravimetric procedure. After the arsenate has been added, it is immaterial how long the determination stands before filtering. Let stand over night,<sup>1</sup> filter and wash thoroughly with dilute ammonia water. The precipitate is then transferred to a 300 to 500 cc. Erlenmeyer flask. If a paper filter has been used, the quantitative transfer is most conveniently made by spreading the paper out on the inner surface of a 4-inch funnel, of which the stem has been bent to rest against the inner wall of the flask into which it has been inserted. The precipitate is rinsed off with hot water, then with dilute acid.<sup>2</sup> Add 10 cc. sulfuric acid (1 acid to 1 water), make up to about 75 to 80 cc. and titrate hot with permanganate solution. Let cool and add 25 cc. more of the acid. It is well not to have the bulk of the solution much over 125 cc. when about to titrate the magnesia; still, if much lime is present, the 75-80 cc. mentioned above may not be sufficient, in which case, a larger bulk and more acid can be used. These proportions of acid are necessary in order to give a satisfactory end point. Add 5 grams of potassium iodide<sup>3</sup> and immediately titrate to a straw color with sodium thiosulfate. Stopper the flask, and cover with black paper, or set in the dark for about 5 minutes. Eight minutes should elapse between the putting in of the iodide and the last part of the titration. Complete the titration drop by drop. Read the end point and place in the dark for one minute. If there is a return of color, discharge it. Usually there will be none if the last drops of thiosulfate have been added slowly. The writer strongly concurs in what Frankforter and Lillian Cohen<sup>4</sup> say about the use of starch, namely, that it is very much better to do without it. The writer tried four samples of starch, and was unable to obtain any satisfactory end point at all. Methylene blue is also useless as an indicator in the strong acid solution. There is no indefiniteness in the end point when simply the fading out of the brown color of iodine is depended on.

The amount of acid prescribed will be found sufficient when amounts up to 40 to 50 cc. tenth normal thiosulfate solution are required. If more magnesia is present, more acid must be added, which can even be done during the titration if done carefully. It is much better, however, to use a stronger solution of

<sup>1</sup> Bull. 422, U. S. G. S., page 119.

<sup>2</sup> Hillebrand, *loc. cit.*, p. 128.

<sup>3</sup> From a qualitative experiment, it appears to be practicable to precipitate the calcium, add tartaric acid, make alkaline, and precipitate the magnesia with arsenate, the iron and alumina remaining in solution in the well-known combination with alkaline tartrate. Some other hydroxy organic solvents for iron oxide were tried, *e. g.*, sucrose and mannite, but did not work so well. No quantitative experiments were made in this direction. This plan would be convenient where iron and alumina are not wanted, or are determined on separate portions of the material.

<sup>4</sup> The precipitation of calcium in acid solution yields larger crystals, as many authors have mentioned, and free from material contamination by occluded magnesia.

<sup>1</sup> One determination gave good results after being shaken twenty minutes after cooling, and immediately filtered.

<sup>2</sup> If too strong acid is used, the filter paper is acted on, giving presumably a cellulose hydrolysis product, which produces a color with iodine. If 50 cc. strong sulfuric acid (sp. gr. 1.84) are mixed with 500 cc. water, and the mixture applied at water bath temperature, all the precipitate will be promptly dissolved and the filter paper not attacked.

<sup>3</sup> If much magnesia is present, it is well to add the potassium iodide slowly, as otherwise a precipitate sometimes falls out which does not readily redissolve. Its composition was not studied.

<sup>4</sup> *Loc. cit.*

thiosulfate, say fifth normal. One cubic centimeter tenth normal thiosulfate solution equals theoretically only 0.002016 magnesia (MgO), so that a fifth normal solution would not be unduly strong. Apply a correction for iodine set free by the light, etc., by titrating as described above 10 cc. and 20 cc. of a solution of ammonium arsenate (of which the exact concentration need not be known—about 20 grams to liter is convenient). If 10 cc. required  $x$  cc. thiosulfate and 20 cc. required  $y$  cc., then the correction is  $(2x - y)$  cc.

It is very important, as the experiments cited show, to standardize the volumetric solutions by weighing out and titrating some suitable compound for the permanganate, pure Iceland spar,<sup>1</sup> and for the arsenate, specially prepared magnesium oxide, or some samples of magnesium ribbon. Very considerable errors will be made by assuming the theoretical values for the solutions.

The following results were obtained:

	CaO taken Grams	Permgt. Cc.	CaO found Grams	MgO taken Grams	Thio- sulfate Cc.	MgO found Grams	Error in MgO
1.....	0.0517	18.70	0.0527	0.0391	18.32	0.0380	-1.1
2.....	0.0517	18.40	0.0518	0.0781	37.31	0.0774	-0.7
3.....	0.0517	18.38	0.0518	0.1172	56.63	0.1174	+0.2
4.....	0.1292	45.97	0.1295	0.0391	18.49	0.0383	-0.8
5.....	0.1292	45.94	0.1294	0.0781	37.38	0.0775	-0.6
6.....	0.1292	45.86	0.1291	0.1172	56.17	0.1165	-0.7
7.....	0.1292	45.90	0.1292	0.0977	47.36	0.0982	+0.5
8.....	0.1292	45.92	0.1293	0.0977	46.48	0.0964	-1.3
9.....	0.1292	45.64	0.1285	0.0977	46.42	0.0962	-1.5
10.....	0.1292	45.72	0.1287	0.0977	48.00	0.0995	+1.8
11.....	0.1292	45.67	0.1286	0.0977	47.93	0.0994	+1.7
12.....	0.0517	18.42	0.0519	0.1953	95.36	0.1977	+2.4
	1.2404	440.52	1.2405	1.1526	555.85	1.1525	-6.7
							+6.6

The results of the titration of calcium call for no special remark. With regard to the magnesium, it may be stated at once that the writer was unable to obtain the very exact results reported by Meade. Meade, however, worked under ideal conditions as to the composition of his solutions, while the results here set forth were obtained under the conditions existing in actual analysis. The writer's results are, however, comparable with those of Frankforter and Lillian Cohen. In cases of this kind we do better to consider the absolute rather than the relative error. The results of the latter are reported in parts per million of Mg, having been obtained from water analyses in which 500 cc. water were used. Thus the results must have been multiplied by two. In the writer's results, as previously mentioned, the standard for the volumetric solutions is taken from the mean of all titrations, while the volumetric results of Frankforter and Lillian Cohen are in the mean 3.3 per cent higher than their gravimetric results. If we make the results of Frankforter and Lillian Cohen comparable with those of the writer by dividing by two, converting Mg into MgO and adding 3.3 per cent to each gravimetric result, we find that the average error amounts to 1.7 mg. MgO in 84.1 mg. MgO, and that the maximum error amounts to 6.5 mg. MgO in 131 mg. MgO. In the writer's results the average error amounts to 1.1 mg. MgO in 96.0 mg. MgO, and the maximum error to 2.4 mg. MgO in 195.3 mg. MgO. It will

<sup>1</sup> Hillebrand, *loc. cit.*

be noticed that the writer's results would be improved by standardizing at two different concentrations. The irregularities seem to be due to a lack of absolute uniformity in the composition of the magnesium ammonium arsenate.

There seems to be no limit in reason to the amount of magnesium which may be titrated, if the concentration of the acid is kept sufficient, but the strength of the thiosulfate solution should be so adjusted—and the principle is, of course, valid in all volumetric work—that not more than 30 to 50 cc. are used in a titration. If it is not so adjusted, the addition of the considerable volume of thiosulfate solution used in the titration so reduces the acid concentration that a good end point cannot be obtained.

The permanganate was standardized with Sørensen's sodium oxalate as supplied by the Bureau of Standards and was found to be 0.0996 normal, which would amount to 0.002794 CaO per cc. For the 440.52 cc. of permanganate used in all the titrations, we should have 1.2309 grams CaO, instead of 1.2404, which would correspond to a loss by solubility of 0.79 mg. per determination. The conditions of each experiment were kept uniform. The thiosulfate solution was standardized by twice sublimed iodine and by permanganate, both according to the directions in Treadwell and Hall.<sup>1</sup> It was found to be 0.1011 normal, corresponding to 0.002038 MgO per cc. or a total of 1.1328 grams MgO instead of 1.1526. This would correspond to an average loss of 1.65 mg. MgO per determination. Whether this loss is caused by solubility or by the magnesium ammonium arsenate as precipitated not corresponding to its formula on the average, the writer does not know. These figures are given to emphasize the necessity of standardizing the volumetric solutions with the same substances and under the same conditions as are used in practice.

This method of determining calcium and magnesium is obviously not adapted to use in making *complete* rock analysis, nor is any volumetric method.<sup>2</sup>

Outside of technical uses, there are many cases in soil and rock work where only partial analyses are desired. For example, in a very interesting article by E. S. Bastin,<sup>3</sup> it is shown how chemical composition serves as a criterion for identifying metamorphosed sediments. Substantially the only elements considered are iron and alumina, and the ratios MgO:CaO and K<sub>2</sub>O:Na<sub>2</sub>O. It is believed that the present method would be useful in this sort of work, especially where it is desired to make a large number of determinations. It is also to be noted that sodium and potassium may be determined in the filtrate from the precipitation of calcium and magnesium, the arsenic being volatilized by means of hydrobromic acid as shown by Browning and Drushel.<sup>4</sup>

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<sup>1</sup> Page 602ff, Vol. II. The standardization by permanganate agrees well with that by iodine, and is much more convenient, even if the permanganate itself has to be standardized with sodium oxalate.

<sup>2</sup> Hillebrand, *loc. cit.*, p. 121.

<sup>3</sup> *Journal of Geology*, **17**, 445 (1909).

<sup>4</sup> *Am. J. Sci.*, **23**, 293 (1907).