DETERMINATION OF SILICIC ACID BY VOLUMETRIC METHOD.

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Determination of silicic acid has hitherto been executed by making in usual ways a solution of the sample to be analysed, by evaporating the solution with hydrochloric or nitric acid, and by weighing the resulting silicon dioxide. In the determination of a minute quantity of the same, the yellow colour of ammonium silicomolybdate is conveniently utilized by comparing it with the colour of a standard solution having the same constituents and containing a known quantity of silicon.(1) Ammonium silicomolybdate can be prepared from an acetic or a sulphuric acid solution of silicate and a solution of ammonium molybdate. In case the comparison of the two colours is unfavourable and does not give accurate results, a solution of benzidine or stannous chloride is added to the yellow solution of the ammonium silicomolybdate and the resulting colour of benzidine blue or molybdenum blue is used for the comparison, so that the determination of a very minute quantity of silicic acid can be made readily.

The yellow compound described above appears usually in solution when acid solutions of ammonium molybdate and silicate are mixed together. With a view to arriving at an easy and accurate method of determination of silicic acid, experiments have been made by the present author to see whether or not this compound can be separated in the form of a precipitate containing all of silicic acid present in the original solution. They have shown that silicic acid can be separated in the form of precipitate by a method which has not been used up to now, and that the same acid can be determined by a volumetric method. A detailed account on this subject being expected to be issued from The Institute of Physical and Chemical Research, Tokyo, outlines only are here presented.

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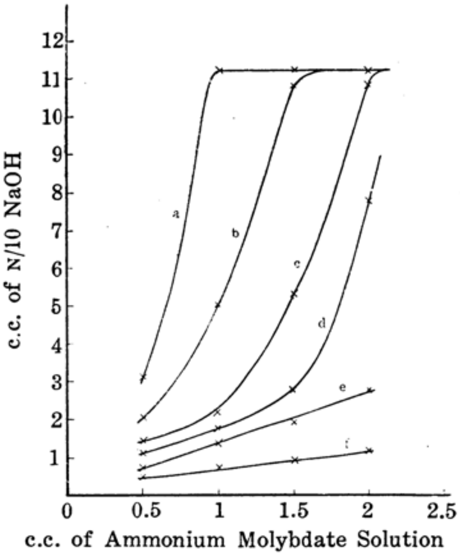
(1) F. Diénert and F. Wandenbulcke, *Compt. rend.*, **176** (1923), 1478; *Bull. soc. chim.*, [4], **34** (1923), 1131. Atkins and Wilson, *Biochem. J.*, **20** (1923), 1223. Isaac, *Bull. soc. chim. biol.*, **6** (1924), 157. Foulger, *J. Am. Chem. Soc.*, **49** (1927), 429. F. J. King and C. C. Lucas, *J. Am. Chem. Soc.*, **50** (1928), 2395. Oberhanser and Schormüller, *Z. anorg. allgem. Chem.*, **178** (1929), 381. F. Feigl und P. Krumholz, *Ber.*, **62** (1929), 1138. F. Feigl, *Z. anal. Chem.*, **77** (1929), 299. W. F. Hillebrand and G. E. F. Lundall, "Applied Inorg. Analysis," (1929), 540. F. Feigl, "Qualitative Analyse mit Hilfe von Tüpfelreaktion," (1931), 310.

The present author has once made studies on the suitable conditions for the complete precipitation of ammonium phosphomolybdate, and found that the concentration of nitric acid, ammonium nitrate, and ammonium molybdate had important effects on the precipitation.⁽²⁾ In the same manner, he has

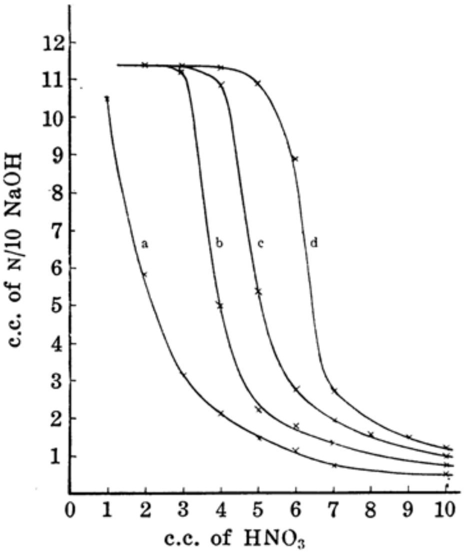
Table 1.

Quantity (g.) of ammonium nitrate added	Quantity (c.c.) of N/10 NaOH solution required for the titration of the yellow precipitate		
	When 3 c.c. of HNO_3 and 1 c.c. of the ammonium molybdate solution were used	When 4 c.c. of HNO_3 and 1 c.c. of the ammonium molybdate solution were used	When 5 c.c. of HNO_3 and 1.5 c.c. of the ammonium molybdate solution were used
0	0	0	0
1	0	0	0
3	10.15	4.48	4.36
5	11.31	5.05	6.37



a: NH_4NO_3 5 g., HNO_3 3 c.c.
b: ,, ,, ,, 4 ,,
c: ,, ,, ,, 5 ,,
d: ,, ,, ,, 6 ,,
e: ,, ,, ,, 7 ,,
f: ,, ,, ,, 10 ,,

Fig. 1.



a: NH_4NO_3 5 g., Ammonium molybdate sol., 0.5 c.c.
b: ,, ,, ,, 1.0 ,,
c: ,, ,, ,, 1.5 ,,
d: ,, ,, ,, 2.0 ,,

Fig. 2.

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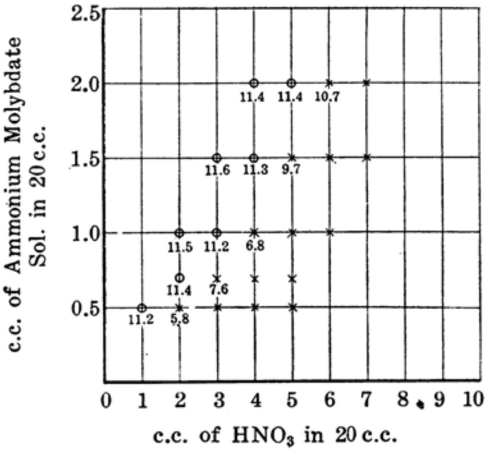
(2) S. Kitajima, *Sci. Pap. Inst. Phys. Chem. Research, Japan,* **16** (1931) 285; *Bull. Inst. Phys. Chem. Research, Japan,* **10** (1931), 65.

recently found that the increase in the concentration of ammonium nitrate and molybdate decreases the solubility of the yellow precipitate of ammonium silicomolybdate, and that when the concentration of nitric acid is increased within a certain limit, the solubility of the yellow precipitate is increased, but when the concentration of the same is increased beyond the same limit, silicic acid tends to separate itself and not to form the yellow precipitate, so that the determination of silicic acid becomes impossible. An example showing the conditions for the precipitation is given in Table 1 and Figs. 1 and 2.

Reagents employed in the experiments were as follows: nitric acid sp. gr. 1.379, about 13.4 N; ammonium nitrate solution contained 1 g. of the repeatedly recrystallized salt in 1.5 c.c. of the solution; ammonium molybdate solution contained 0.232 g. of molybdenum in 1 c.c. and was made by dissolving 50 g. of the salt in 100 c.c. of dilute ammonia solution obtained from 1 volume of concentrated ammonia (sp. gr. 0.9) and 3 volumes of water. The sodium silicate solution was made by dissolving about 1% anhydrous sodium silicate and confirmed by gravimetric method to contain 0.0622 g. of SiO_2 in 10 c.c.

Various quantities of the sodium silicate solution, water, the ammonium molybdate solution, the nitric acid, and the ammonium nitrate solution were taken in succession into an Erlenmeyer flask having a glass stopper, so as to make the total volume of the mixture just 20 c.c. The mixture was shaken and allowed to stand in a bath of about 70° for one hour. The yellow precipitate was collected, washed, and titrated with N/10 NaOH solution, phenolphthalein being employed as indicator. In the filtration and washing, various sorts of filters were employed, and the precipitate was found to be liable to come more or less into the washings, in every case where filter paper was used. Glass filters having fine pores were found to be most suitable for washing. Aqueous solutions of nitric acid, potassium nitrate, ammonium nitrate, and other salts in varying concentrations were separately employed in washing the precipitate in order to avoid its passing through the filter without success. A solution of 15% NH_4NO_3 and 0.02% HNO_3 (about 0.00027 N in HNO_3) was finally found to be most suitable for the washing purpose.

Various known quantities of the sodium silicate solution were taken, and silicic acid was precipitated as yellow ammonium silicomolybdate by the method described above by using varying quantities of the reagents. The precipitates were titrated with a standard NaOH solution. Among various values obtained by the titration, there were found a number of the largest and identical ones. Out of these values and those showing the concentrations of the reagents in the solutions, in which the yellow precipitates formed, a diagram shown in Fig. 3 has been made, which shows the interdependence of the reagents in the complete precipitation of silicic acid.



The diagram in Fig. 3 shows perfect and imperfect precipitation of ammonium silicomolybdate in the mixed solutions containing 0.1 c.c. of the sodium silicate solution, 5 g. of NH_4NO_3, and the varying quantities of HNO_3 and ammonium molybdate given in the diagram. Here, the mark ○ indicates complete, and × incomplete, precipitation. Figures given below the marks show the number of c.c. of N/10 NaOH solution required for the titration of the precipitates.

Fig. 3.

That the largest and identical value described above corresponds to the correct value of silicic acid has been confirmed as follows. The mixture resulting from the titration was transferred to a casserole, evaporated to a volume of about 10 c.c., and then heated with 6–10 c.c. of concentrated sulphuric acid until white fume of the acid was vigorously given off. The residual solution was diluted with 50 c.c. of water. The insoluble silicic acid was collected, washed thoroughly, transferred to a crucible, ignited, and weighed, the weight of silica being found to correspond to the quantity of the silicate contained in the original solution.

The quantity of silicic acid present in the yellow precipitate being considered by the author to be determinable also by reducing the molybdic acid present in the same precipitate to a lower compound and by titrating the latter with an oxidizing agent, experiments have been made as follows. The final solution of the titration was evaporated in a casserole to a volume of about 10 c.c., and heated with 6–10 c.c. of concentrated sulphuric acid until white fume was given off and the liquid became blue. The residual solution was diluted with 50 c.c. of water, shaken with zinc amalgam, and titrated with N/10 $KMnO_4$ solution. The experiments have shown that this method gives accurate results more readily than that of the titration with sodium hydroxide.

A few examples of the determination of silicic acid actually made by gravimetric method and by volumetric method using both NaOH and $KMnO_4$ are given in Table 2.

Table 2.

I	II	III	IV	V	VI	VII
Quantity of the sodium silicate solution taken (c.c.)	Quantity of SiO_2 contained in the sodium silicate solution (g.)	Quantity of the N/10 NaOH solution used in the titration (c.c.)	Number obtained by dividing tne number under II by the corresponding number under III	Quantity of SiO_2 determined by gravimetric method (g.)	Quantity of the N/10 $KMnO_4$ solution used in the titration (c.c.)	Number obtained by dividing the number under II by the corresponding number under VII
5	0.03106	112.60	0.000275			
3	0.01863	68.73	0.000271			
2	0.01242	45.90	0.000270			
1	0.00621	22.59	0.000274			
1	0.00621	22.54	0.000275			
2.5	0.01553	56.53	0.000274	0.01616	103.2	0.000166
0.5	0.00310	11.50	0.000270	0.00338	18.5	0.000167
0.5	0.00310	11.31	0.000274	0.00302	18.6	0.000166
			0.000273			0.000166

As shown in column IV in Table 2, the mean was found to be 0.000273. This number is justified to be a factor, by which the numbers given in column III showing the quantities of the NaOH solution in c.c. are multiplied in order to find the quantities of SiO_2; namely, c.c. of N/10 NaOH × 0.000273 = g. of SiO_2. Just in the same way the numbers in column VI are multiplied by the mean, 0.000166, in order to obtain the quantities of SiO_2; namely c.c. of N/10 $KMnO_4 \times 0.000166$ = g. of SiO_2.

The following conclusions have thus been obtained: (1) From a solution of silicate, silicic acid can be completely precipitated as ammonium silicomolybdate of yellow colour. (2) Concentration of each of nitric acid, ammonium nitrate, and ammonium molybdate suitable for complete precipitation of the yellow compound has been found experimentally. (3) The quantity of silicic acid present in the yellow precipitate can be determined either by titrating the precipitate with sodium hydroxide, or by reducing molybdic acid present in the precipitate to a lower compound and by titrating the latter with potassium permanganate. (4) Silicic acid can also be determined by gravimetric method, from the yellow precipitate or from the solution resulting from the titration with sodium hydroxide or potassium permanganate.

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