STUDY OF THE YELLOW SILICOMOLYBDATE COMPLEX IN AQUEOUS SOLUTION

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The formation and stability of yellow silicomolybdic acid, which is the basis for the colorimetric determination of silica, has been studied, in relation to factors like temperature, reaction time, acidity and reagent concentrations. Results show that, when these factors are controlled within reasonable limits, fairly satisfactory results are obtained.

Introduction

The yellow heteropoly acid, the 12-silicomolybdic acid, forms the basis for a colorimetric method for the determination of silicon.[1,2] The blue complex formed by reduction of the yellow one is also used for estimating smaller amounts of the element.[3,5]

A large number of silica determinations are required to be made of various samples of ores, minerals and rocks and the results by the usual gravimetric method (acid dehydration and hydrofluorization) are very satisfactory even in the hands of an inexperienced chemist, but the method is time-consuming and tedious. Though the method for the colorimetric determination of silica is an old one and numerous authors have worked on the problem, no detailed discussions of the factors affecting the result are available.

The present study was undertaken in order to find out the optimum conditions for the formation of the yellow silicomolybdate complex, its stability and behaviour under different conditions. These would in turn indicate the degree of accuracy of the colorimetric method as compared to the gravimetric one, and the advisability of replacing the gravimetric method by the latter.

Experimental

Standard silicate solution was prepared by fusing 0.117 g. of precipitated silica (SiO_2=85% standardized gravimetrically) with 1 g. of sodium carbonate, extracting the mass with water and making up the solution to 500 ml. 1 ml. of the solution=0.2 mg. of SiO_2.

Ammonium molybdate solution, 7.5%, was made by dissolving 18.75 g. of ammonium molybdate (A.R.) in water and adding slowly 22.5 ml. of sulphuric acid (sp. gr. 1.84). A clear solution is obtained, and the volume is made up to 250 ml.

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Method of Studying the Complex Formation.—An aliquot of the standard silicate solution is pipetted into a 50 ml. measuring flask. Acidic ammonium molybdate solution (10 ml.) is then added with stirring and the flask transferred to a thermostat and reaction allowed to continue for the desired time. The flask is withdrawn and cooled to below 30°C. in tap water. The volume is made up to 50 ml. and the absorbancy measured in the single cell Hilger's photometer (H 810.301) with filter No. 43 (equivalent to 430 mμ) using a glass cell approximately 1 cm. thick against reagents blank, set to zero.

Results

Effects of Temperature and Time.—Temperature and time of reaction affect considerably the development of the yellow colour and its stability. Mixtures of sodium silicate and ammonium molybdate in the optimum condition of acidity were heated with occasional stirring for various durations ranging from 15 seconds to 1 hour and at a temperature varying from 20° to 100°C.

It is seen that at lower temperatures up to 50°C., the reaction reaches a maximum and remains fairly stable with only a slight change in intensity, whereas at higher temperatures the reaction is rapid, it reaches a maximum and falls off rapidly to a much lower value (Figs. 1 to 5).

The maximum colour developed at different

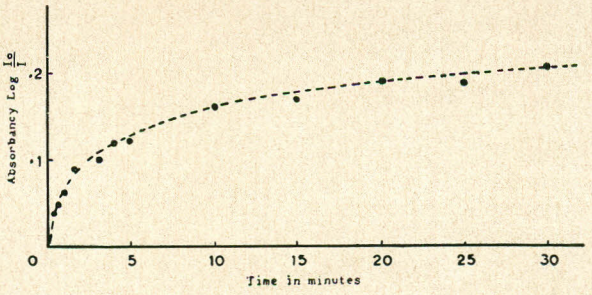

Fig. 1.—Reaction with 2.0 mg. of SiO_2 with 10 ml. of 7.5% ammonium molybdate at 30°C.

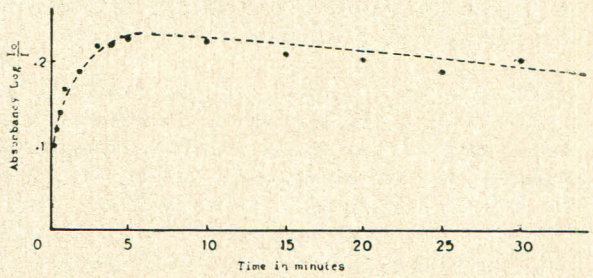

Fig. 2.—Reaction with 2.0 mg. of SiO_2 with 10 ml. of 7.5% ammonium molybdate at 50°C.

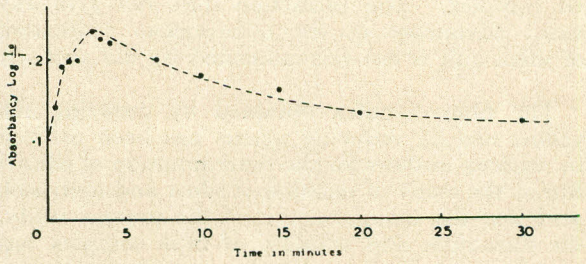

Fig. 3.—Reaction with 2.0 mg. of SiO_2 with 10 ml. of 7.5% ammonium molybdate at 60°C.

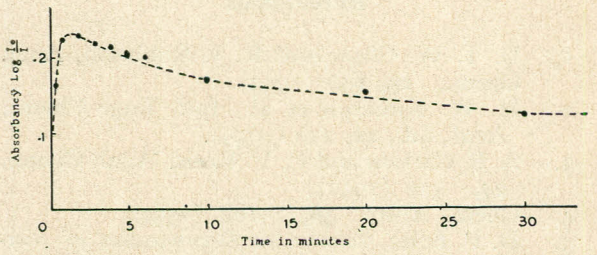

Fig. 4.—Reaction with 2.0 mg. of SiO_2 with 10 ml. of 7.5% ammonium molybdate at 80°C.

temperatures is not, however, the same, the best value being obtained at temperature near 50°C. At lower temperature, the values were lower and at higher temperature, the values are either the same or a bit higher but they decrease quite rapidly.

The most favourable temperature for the reaction was, therefore, fixed at 50°C. for a period of 5 minutes. The colour intensity remains stable when the reaction mixture is brought to a temperature below 30°C.

Optimum Concentration of Reagent.—A large excess of acidic ammonium molybdate is required for maximum colour formation. A plot of mole ratio of MoO_3:SiO_2 (Fig. 6) maintaining a constant concentration of SiO_2 shows that about 20 moles of MoO_3 are required for each mole of SiO_2, and the curve fairly obeys Beer's law.

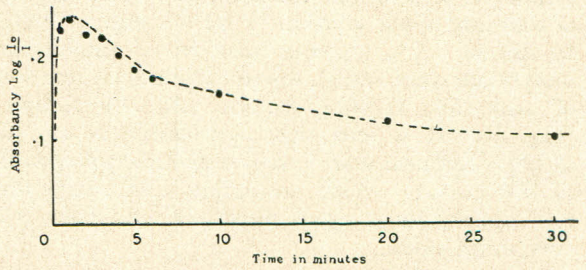

Fig. 5.—Reaction with 2.0 mg. of SiO_2 with 10 ml. of 7.5% ammonium molybdate at 90°C.

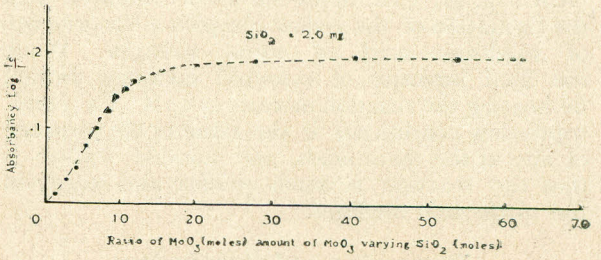

Fig. 6.—Absorbancy vs. reagent concentration.

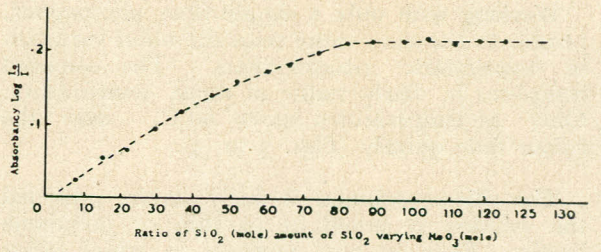

Fig. 7.—Absorbancy vs. silica concentration (calibration curve).

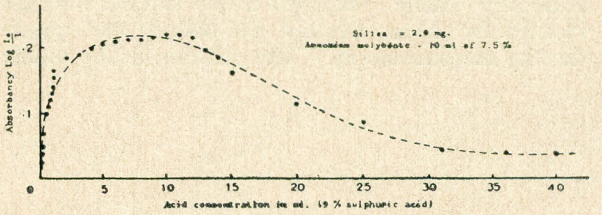

Fig. 8.—Absorbancy vs. acid concentration.

Similarly a plot of mole ratio of SiO_2/MoO_3 maintaining a constant concentration of MoO_3 shows a similar curve (Fig. 7). Incidentally, Fig. 6 points out that molybdenum can also be estimated colorimetrically by adding an excess of silicate solution to a solution of ammonium molybdate in acid.

Optimum Acid Concentration.—It has been observed that no coloured silicomolybdic acid is formed in alkaline solution. In order to determine the effect of increasing acid concentration on the

formation of coloured complex, to 10 ml. aliquots of standard silica solution (1 ml.=2 mg. of SiO_2) 10 ml. of 7.5% aqueous solution of ammonium molybdate were added, followed by known amounts of acid (9% H_2SO_4, sp. gr. 1.84, by volume) (Fig. 8). It is seen that approximately 10 ml. of 9% sulphuric acid is required for development of full colour. With increasing acid concentration the colour is again depressed and falls to a very small value.

Acids Other Than Sulphuric Acid.—The effect of using nitric (A.R., sp. gr. 1.42) and hydrochloric (A.R., sp. gr. 1.18) acids has been compared with the formation of the yellow complex in the presence of sulphuric acid of equal strength. While the final intensity of coloured complex formed by heating the reaction mixture at 50 °C. for 5 min. (optimum conditions) is the same in the presence of any of the three acids, one notable feature is that the reaction is much quicker and steady in the nitric acid medium.

Discussion and Conclusion

Working with only a simple filter photometer, results do not show more than the usual variation in colorimetric measurements. The coloured complex is fairly stable at room temperature. Only at temperatures above 60°C. does the colour fade quickly (Figs. 3 to 5).

The silicate solution is fairly stable, provided the solution is stored in paraffin or polythene bottles. Even in acid medium in which silica is made to react with ammonium molybdate, it is quite stable. Storage of the silicate solution in acid for seven days did not change the optical density measurements. The solution is also stable at higher temperature provided a proper acid concentration is maintained.

The coloured complex can be extracted in organic solvents.[4] With ether only it was seen that partial extraction could be made in strong acid medium. Even three successive extractions could not give more than 90% of the original colour intensity. However, a mixture of ethyl acetate, butyl alcohol and chloroform in the proportion of 1:1:4 in the presence of 0.7 N nitric acid, efficiently extracts the coloured complex[6] and absorbancy measurements give the same results for the extracted complex. The extraction does not give any extra advantage in the colorimetric estimation of silica and is not recommended by the authors.

The blue complex obtained by reducing the yellow one by reducing agents has been utilized by various authors for the determination of silica.[3] But as the study of reaction of silica and molybdic acid was the main concern of the present study, the formation and stability of blue complex has not been studied in the present investigation, which may be taken up in future.

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