Studies in the Determination of Silica

I. Spectrophotometric Determination of Silica as α-Silicomolybdate

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A modified silicomolybdate method is described, which is shown to be uninfluenced within wide limits by variables such as pH, molybdate and salt concentrations. The colour produced is stable for long periods of time, and extinction measurements are reproducible with good precision. The reason for these improved properties is that the stable α-silicomolybdate is used instead of the unstable β-compound.

Since the discovery in 1898 by Jolles and Neurath[1] that the reaction between silica and molybdate in water solutions to form yellow silicomolybdic acid could be used for analytical purposes, much work has been devoted to the study of this colorimetric method for silica determination. It was not until the introduction of accurate spectrophotometers, however, that more thorough investigations could be undertaken, and since about 1930 many papers dealing with the subject have been published. Despite this no definite solutions of the problems concerned have been presented, and as recently as 1952 Strickland[2] published a series of papers dealing with the preparation and properties of silicomolybdic acid. Stoll[3] and Lacroix and Labalade[4] had made more restricted experiments. The papers by Mellon[5], Mullin and Riley[6] and Arnfelt *et al.*[7] summarize and give references to the earlier literature as well as to more modern works.

Strickland's[2] most important contribution seems to be his discovery that silicomolybdic acid occurred in two forms, of which the one called β was more or less rapidly converted to the stable α-form under normal temperature and pressure. On the basis of his results he recommended the unstable β-form as suitable for analytical purposes.

Although almost all reactions involved in the formation of the silicomolybdic acids probably are very complicated, the following scheme will give a rough idea of the processes taking place in water solution:

$$\underbrace{\text{molybdate ions} + \text{silicate ions}}$$

β-silicomolybdate ions $\longrightarrow$ α-silicomolybdate ions.
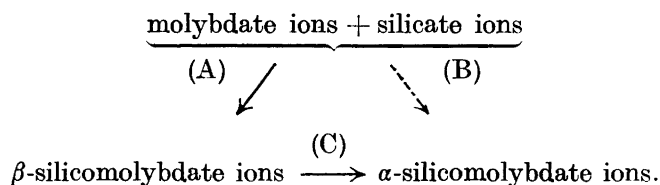
It is not known if reaction (B) actually takes place. The molybdate as well as the silicate ions are to a certain degree polymerised, the degree of polymerisation varying with the composition of the solution. Lindqvist [8] gives the following scheme for the reactions occurring when a molybdate solution is acidified:

$$MoO_4^{2-} \rightarrow Mo_7O_{24}^{6-} \rightarrow Mo_8O_{26}^{4-} \rightarrow \text{larger complexes}$$

An attempt to study the influence of silicate polymerisation was made by Chow and Robinson [9].

In the present paper a few experiments with the earlier silicomolybdate method will be described, which show important drawbacks connected with it. After that a modified method is presented together with an investigation of the influences on that method of some important factors. Interferences from phosphorus, arsenic and germanium as well as from iron and aluminium and fluorine will be dealt with in later papers.

1. EXPERIMENTAL DETAILS

The chemicals used were of analytical grade. Distilled water for the preparation of solutions had not previously been in contact with glass, but was taken from a distillation apparatus with metal parts. All solutions were stored in polythene bottles. Ammonia solutions were prepared by dissolving tank ammonia in distilled water.

Two different preparations of silicic acid were used: one was a commercial chemical (Baker) and the other had been prepared from sodium silicate by a method similar to that used in the ordinary silica separation procedure. Both chemicals were analysed for their water contents by heating samples to constant weight in platinum crucibles, and for their silica contents by treatment with hydrofluoric and sulfuric acid, followed by heating to constant weight; the residues did not exceed 0.2 % of the amount SiO_2 taken.

The dissolution process was accomplished by fusion with Na_2CO_3 in a platinum crucible, and then digesting its contents with water in a platinum dish. In some cases the silicic acid was placed in a platinum dish together with 4 g NaOH and a few ml of water and dissolution carried out by heating on the steambath. However, solutions prepared in this last way always showed low values (by 1—2 %) compared with those prepared in the first way, which were therefore generally preferred.

Blank solutions were prepared in a manner similar to that used for the corresponding silica solutions. They were employed in the preparation of blanks and, when necessary, for diluting the standard silica solutions.

A Beckman model DU spectrophotometer, the cuvette compartment of which was maintained at a constant temperature (20.0°C unless otherwise stated), was used for all extinction measurements. The same set of three numbered cuvettes were used, the first being filled with distilled water, the second with the blank and the third with the coloured solution. A correction for their different optical properties was applied. The instrument was checked with respect to the wavelength scale (using a mercury lamp) and the extinction scale (using a K_2CrO_4 solution as described by Haupt [10]).

pH measurements were carried out with a Beckman model H 2 instrument using a glass electrode and a saturated calomel electrode. 0.05 M KH-phthalate (pH = 4.0) and 0.100 M HCl (pH = 1.1) were employed as reference solutions.

2. EXPERIMENTS WITH EARLIER METHODS

Previous methods have been tested with respect to certain variables and have turned out to be unsatisfactory in different ways. A desription of an experiment designed to furnish the extinction as a function of time at different NaCl concentrations in the solutions used will demonstrate an important property of the silicomolybdic acid system.
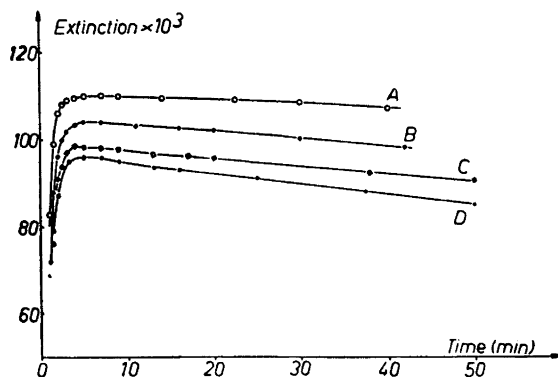
Fig. 1. Extinction-time dependence for earlier method with [NaCl] as a variable.
A, [NaCl] = 0; B, [NaCl] = 0.4 M; C, [NaCl] = 0.8 M; D, [NaCl] = 1.2 M.

Of two 100 ml beakers, one was filled with 25 ml of a molybdate solution (0.04 M in Na$_2$MoO$_4$, pH = 1.5 with HCl) and the other with 25 ml of silica solution (8 mg Si/l, pH = 1.5 with HCl; appropriate amounts of NaCl added). The two solutions (20.0°C) were quickly mixed and the mixture transferred to a 1 cm cuvette. With the aid of two stopwatches, which were alternately stopped and started just at the instants the moving (the extinction was changing!) meter needle of the DU instrument indicated balance at a preset extinction value, the extinction as a function of time was obtained.

In Fig. 1 curves are given for different NaCl concentrations in the final solutions. It can be seen that the optical properties of the system are strongly influenced by NaCl additions. Actually the effect of salts containing divalent anions such as Na$_2$SO$_4$ is still more pronounced.

It follows from this and similar experiments with other salts that pH as well as molybdate concentration influences cannot be treated as independent variables and without reference to the salt content of the solutions. Factors which affect the composition of the final solution to be analysed for silica by this method must be carefully controlled.

3. A MODIFIED METHOD

If the reaction

$$\beta\text{-silicomolybdate} \rightarrow \alpha\text{-silicomolybdate}$$

is allowed to proceed completely to the right a stable yellow colour is obtained. At room temperature the reaction rate is comparatively low but is accelerated by salt additions. When the solution is heated on a steam bath the conversion is practically complete within about 3 h, the actual time being dependent on the composition of the solution in question. On this basis the following general procedure has been worked out which, with appropriate modifications, was used in the following experimental work unless otherwise stated.

The solution to be analysed is mixed with a molybdate solution in a polythene bottle and the bottle is placed on the hot steambath. After the appropriate time interval the bottle with contents is cooled to 20.0°C, transferred to a volumetric flask, made up to volume with water or a suitable solution and mixed. The extinction is measured against a blank which has been treated in an analogous way.
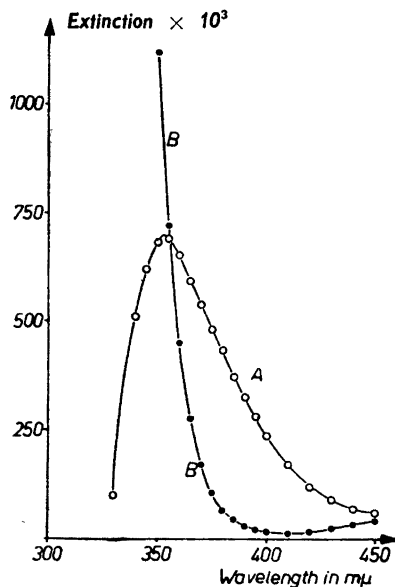
Extinction × 10³

1000

750

500

250

B

A

B'

300   350   400   450

Wavelength in mμ

Fig. 2. Extinction as a function of wavelength. Curve A, α-silicomolybdate solution measured against the blank; B, blank measured against water.

Using this procedure the modified method was tested with respect to some important variables. Unless otherwise stated the solutions when heated on the waterbath have a volume of 20 ml, which is later diluted to the final volume, 25 ml.

3. 1. The extinction as a function of wavelength

The measurements were performed with solutions which when heated on the steambath were 0.25×10^{-3} M in Si and 0.05 M in Na_2MoO_4, with a pH of 1.5, adjusted with perchloric acid. The heating time was long enough to ensure a complete conversion to α-silicomolybdate.

In Fig. 2 is plotted the extinction-wavelength curve for α-silicomolybdate (A) and for the blank (B). The yellow complex has an extinction maximum at about 350 mμ, but at this wavelength the blank absorbs strongly. A longer wavelength should be chosen, where the blank absorbs little light compared to the solution containing silica. This is all the more necessary because the light absorption of acidified molybdate solutions depends on their pH, especially at shorter wavelengths [11]. At 400 mμ, a wavelength which has been found suitable for most purposes, the absorption due to the molybdate ion species is small and in practice independent of small pH fluctuations.

It is clear from Fig. 2 that at 400 mμ the rate of change of extinction with wavelength is numerically large. This has two consequences: it is necessary to control the wavelength setting carefully to obtain reproducible extinction values between different series of measurements, and good monochromatic light is necessary for a linear relationship between extinction and silica concentration. The corex filter supplied with the Beckman DU instrument should be used to eliminate scattered radiation.
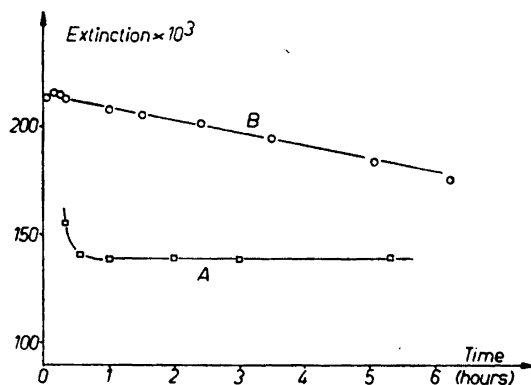
Fig. 3. Extinction-time dependence for solutions treated according to new procedure (curve A) and for solutions which have not been heated.

3.2. Extinction-time dependence

A number of solutions were prepared and put on the water-bath. They were 0.144×10^{-3} M in Si, 0.05 M in Na_2MoO_4 and had a pH value of 1.5, adjusted with perchloric acid. From time to time a bottle was withdrawn from the waterbath, its contents prepared according to the directions and the extinction measured. The result is shown in Fig. 3, curve A; curve B represents an identical solution which has not been heated.

The time within which a constant extinction value is obtained is subject to some variations in practice; three hours are usually enough, but solutions containing, e.g., large amounts of silica seem to require a longer heating time, especially if the pH is low.

3.3. Dependence on pH and salt concentration

The solutions were the same as in 3.2, with the exception, that they contained different amounts of perchloric acid or in a few cases sulfuric acid.
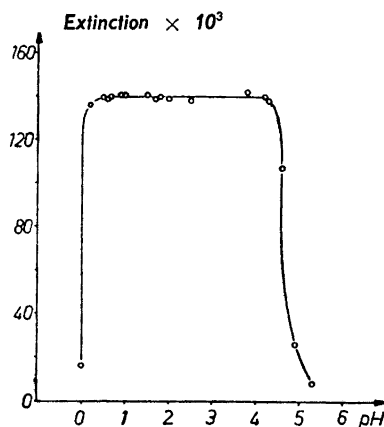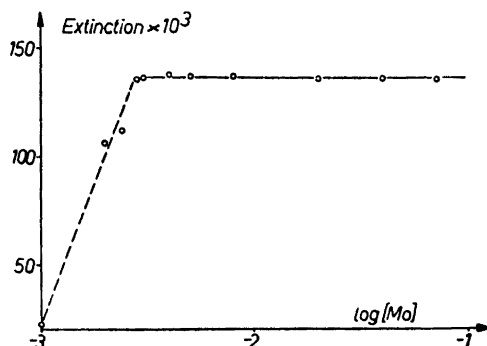

Fig. 4. Extinction as a function of pH.

Fig. 5. Influence of the molybdate concentration.

Included in this series of measurements are also some, which have been made on solutions containing up to 0.2 moles of Na_2SO_4 per litre of final solution.

The optical density as a function of pH is plotted in Fig. 4; the horizontal line represents the mean calculated from 16 experiments. From these a maximal deviation of 1.3 % and a standard deviation of a single measurement of 0.8 % is calculated. (pH for these measurements was confined to the interval $0.5 \leqq pH \leqq 4.3$; the pH values below 1.0 are not very accurate and may well be in error with some tenths of a pH unit.)

3.4. Influence of the molybdate concentration

When treated on the steambath the solutions had the following compositions: 0.144×10^{-3} M in Si, pH in general 2.0 (in a few cases 1.5 and 3.5) adjusted with perchloric or sulfuric acid, the molybdate concentration being variable.

In Fig. 5 is given the extinction as a function of $^{10}log[Mo]$. The minimum amount of molybdate required for a full development of the yellow colour is greater than would be calculated for a ratio [Mo] : [Si] = 12, obtained in the crystallized α-silicomolybdate both analytically [2] and from X-ray work [12].
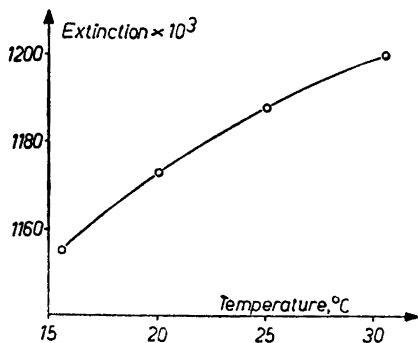

Fig. 6. Extinction as a function of temperature of the solution being measured.

Table 1. Applicability of Beers law to solutions of α-silicomolybdic acid. $k = E/c$; k = extinction coefficient, E = extinction for 1 cm cuvette length, c = molarity of Si.

Number of experiments	$c \times 10^3$	E, mean	$k \times 10^{-3}$		
			mean	max.dev. from the mean, %	Stand.dev. of a single measurement, %
5	1.200	1.461	1.218	0.6	0.4
5	0.900	1.096	1.218	0.5	0.3
5	0.600	0.733	1.222	0.5	0.2
4	0.300	0.366	1.220	0.6	0.5
2	0.120	0.146	1.22		
2	0.060	0.074	1.23		

When solutions which are about 0.2 M in Na_2MoO_4 or higher are heated on a steambath for several hours a white precipitate is often obtained, especially if the polythene bottle used has earlier contained such a precipitate. Solutions which were very concentrated in Na_2MoO_4 and have precipitated large amounts of such a solid phase, have in some cases shown extinction values slightly (about 1—2 %) lower than calculated. However, it has been found perfectly safe to use solutions which when heated are 0.05—0.1 M in Na_2MoO_4 and which may contain so much silica that the resulting extinction is about 1.5, provided no other heteropoly forming ions such as PO_4^{3-}, AsO_4^{3-}, Fe^{3+} and Al^{3+} are present. It might be added that precipitates of the above mentioned type are not easily formed in solutions containing large amounts of sulphate ions.

3.5. Influence of the temperature on the extinction

The solutions used had the following composition when heated on the waterbath: 1.25×10^{-3} M in Si, 0.05 M in Na_2MoO_4, pH = 1.5 with perchloric acid. After complete conversion to α-silicomolybdate the solutions were cooled to 20.0°C and made up to volume with water of the same temperature. Blanks were also prepared quite similarly.

In Fig. 6 the extinction is plotted as a function of the temperature of the solution being measured. No correction for volume changes has been applied. The temperature coefficient is not a constant but a function of temperature; at 20°C the extinction is seen to vary about 0.2—0.3 % per degree C. It may be that with other compositions of the solutions another extinction-temperature dependence can be obtained.

3.6. Applicability of Beers law

The measurements were carried out in the usual manner, great care being taken to ensure that the heating time on the waterbath was long enough.

The results of the measurements are summarized in Table 1. Extinctions for final silica concentrations equal to or greater than 0.3×10^{-3} M have

been measured on solutions subject to slight variations in pH (1.5 and 2.0) and in molybdate concentration (final solutions 0.04 and 0.08 M in Na_2MoO_4); in a few cases Na_2SO_4 was added so that the final solutions were 0.2 M in Na_2SO_4.

REFERENCES

1. Jolles, H. and Neurath, F. Z. angew. Chem. 11 (1898) 893.
2. Strickland, J. D. H. J. Am. Chem. Soc. 74 (1952) 862, 868, 872.
3. Stoll, K. Mitt. Naturw. Ver. Vorpomm. in Greifswald 63 (1936) 1.
4. Lacroix, S. and Labalade, M. Anal. Chim. Acta 3 (1949) 383.
5. Mellon, M. G. Symposium on Structure and Properties of Heteropoly anions, Am. Chem. Soc., Atlantic City 1956, p. 35.
6. Mullin, J. B. and Riley, J. P. Anal. Chim. Acta 12 (1955) 162.
7. Arnfelt, H., Freyschuss, S. and Rönnholm, B. Jernkontorets ann. 135 (1951) 75.
8. Lindqvist, I. Nova Acta Regiae Soc. Sci. Upsaliensis (4) 15 (1954) No. 1.
9. Chow, D. T. and Robinson, R. J. Anal. Chem. 25 (1953) 646.
10. Haupt, G. W. J. Research Natl. Bur. Standards 48 (1952) 414.
11. Carpéni, G. Bull. soc. chim. France [5] 14 (1947) 484.
12. Keggin, J. F. Proc. Roy. Soc. A 144 (1934) 75.