

CRITICAL FACTORS IN THE COLORIMETRIC
DETERMINATION OF SILICA*

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INTRODUCTION

During the course of a comprehensive research programme aimed at a better understanding of the controlling factors in the dissolution of natural silicates and the formation of secondary products in aqueous solution under normal temperature and pressure conditions, it became necessary to undertake a large number of determinations for both soluble and total silica. A brief survey of the literature revealed a large number of analytical methods based upon the formation of silicomolybdate complexes. As routine analyses proceeded, it became clear that lack of understanding of controlling factors and the mechanism of formation of these complexes prevented any adaptation of the method to suit the circumstances and still obtain reliable results. Accordingly, an intensive search of the available literature was undertaken, accompanied by detailed experimental work, to determine the optimum operating conditions. Standard commercial reagent-grade chemicals were used throughout, and hence no great accuracy is claimed for the results presented; moreover, the substance of this paper is only a side-issue of a much more comprehensive project. Inasmuch as geological work is now making increasing demands upon chemical and physical techniques, it is felt desirable to record the results obtained.

Silica in aqueous solution

Silica in "solution" exists in a number of different forms: in the pH range 1-8 and in concentrations less than about 110-140 p.p.m., the stable form is the monomeric molecule $\text{Si}(\text{OH})_4$ ¹; above pH 9 the solubility of amorphous silica rises sharply due to the formation of the silicate ion, thus:



The silicate ion will exist in solution together with $\text{Si}(\text{OH})_4$. At very low pH solubility of silica may be increased by acids, such as HF to form silicofluoride anions. In solutions more concentrated than 110-140 p.p.m. SiO_2 , polymerization occurs giving rise to polysilicic acids, and ultimately a colloid, gel, or a precipitate. Polymerization of two $\text{Si}(\text{OH})_4$ molecules may lead to the formation of dimeric silicic acid where each of the two silicons is surrounded octahedrally by 6 OH ions; further polymerization will lead to the formation of trimeric silicic acid, whilst condensation and elimination of water will lead to branched-chain and ring polymers². Continued increase in size will give rise to the formation of colloidal particles and, under suitable conditions, a gel.

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ILER² states that monosilicic acid is most stable at a pH of 1-3, and least stable between pH 5 and 6. According to ALEXANDER³ monosilicic acid in 0.1 *M* solution at 2° polymerizes almost instantly at pH 6, and is most stable at pH 3.2; the polymerization below pH 3.2 is a third order reaction, giving linear or openly branched polysilicic acid chains, whilst above pH 3.2 the polymerization is a second order reaction and depolymerization-polymerization rearrangement of polymers gives rise to cyclic or cross linked polymers. ALEXANDER³ also stated polysilicic acid diluted to 40 p.p.m. depolymerizes at room temperature at a pH of 1.0, but the rate is slow compared with the rate of polymerization. The rate of polymerization at room temperature of polysilicic acid is approximately proportional to the square of the concentration of silica⁴.

Reaction of silica with molybdic acid

DIENERT AND WANDENBULCKE⁵ in 1923, and HARMON⁶ in 1927, showed that only "soluble" silica will react with molybdic acid to form a yellow silicomolybdate complex, and that colloidal silica is unreactive. This reaction has been the basis of very many colorimetric methods for the quantitative determination of silica, either by measurements of the intensity of the yellow silicomolybdate complex or the reduced blue complex. This reaction was further clarified by WEITZ, FRANK AND SCHUCHARD⁷ who demonstrated that monomeric silicic acid will react completely in about 75 sec, disilicic acid in about 10 min, whilst higher polymers take even longer. This reaction has been confirmed by ALEXANDER⁸ and RICHARDSON AND WADDAMS⁹ although, as seen later, it is only true under certain experimental conditions.

In 1952 STRICKLAND¹⁰ published a series of three papers in which he demonstrated that there exists at least two forms of silicomolybdic acid in solution, both having the formula $H_4(SiMo_{12}O_{40})$ and both yellow in color, but having quite different light-absorbances. The stable form was designated as α -silicomolybdic acid which is the predominant form in solutions acidified with up to 1.5 equiv. of acid per mole MoO_4^{-2} . The other form, β -silicomolybdic acid, is formed in quantity when more than 1.5 equiv. of acid per mole MoO_4^{-2} is present, and the yellow complex has an absorbance of about twice that of α -complex. The β -acid changes spontaneously to the α -form, a change which is hastened when the pH is raised above 2.5, by heating, and in the presence of excess electrolyte. The change is retarded, even under the latter conditions, when molybdate is present in excess of that required to react with silica. STRICKLAND¹⁰ suggested that the β -acid is an unstable polymer of the α -acid, the spontaneous β to α change having the characteristics of an irreversible depolymerization.

Published analytical methods for the determination of silica have been based upon the formation of the β -acid, although there have been two recent methods^{11,12} based upon the formation of the α -complex. Despite STRICKLAND's¹⁰ detailed investigation of the conditions of formation of silicomolybdic acids, his work has been largely ignored or apparently misinterpreted. Most published data place great emphasis upon the pH and give scant attention to the ratio and type of acid to molybdate, nor to the particular species of molybdate added to the reaction — although both of these factors are important as STRICKLAND's¹⁰ work showed. Data are presented in the following paragraphs which confirm or expand some of STRICKLAND's¹⁰ fundamental observations; the conditions to be considered when designing an analytical method for silica to suit particular circumstances are also outlined.

EXPERIMENTAL RESULTS

It has been asserted by RINGBOM *et al.*¹¹ that pH is the major variable determining the development of the yellow silicomolybdate complexes; these writers published an absorbance-pH curve showing a plateau of constant absorbance values between pH 2 and 4 which they equated with formation of α -silicomolybdic acid. The initial experiments were designed to compare the results obtained by RINGBOM *et al.*, who used monochloroacetic acid as the acidifying agency, with results obtained when using sulphuric acid. The same concentration of ammonium molybdate recommended by RINGBOM *et al.* was used, and the change in absorbance was measured at intervals of 2 min to 96 h over the pH range 0.5 to 5.5.

Method

An aliquot of standard SiO_2 solution in a 50-ml volumetric flask was acidified with a suitable mixture of either sulphuric acid and ammonium hydroxide, or mono-

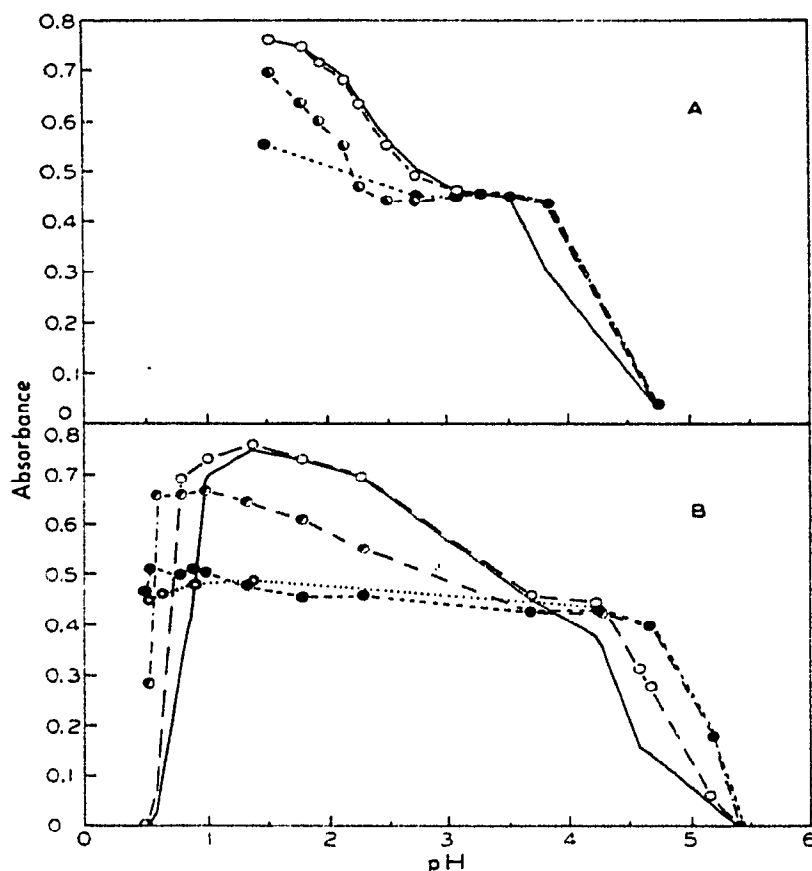


Fig. 1. Variation of absorbance of silicomolybdate solutions due to pH and time, and comparison of results obtained with monochloroacetic acid and sulphuric acid. A, solutions acidified by mixtures of 2 *M* monochloroacetic acid and ammonium hydroxide. B, solutions acidified by mixtures of 1 *N* sulphuric acid and ammonium hydroxide. — absorbance measured 2 min after start of reaction; ○ — ○ absorbance measured 10 min after start of reaction; ● ····· ● absorbance measured 5 h after start of reaction; ● — — — ● absorbance measured 24 h after start of reaction; ◎ ····· ◎ absorbance measured 48 h after start of reaction.

chloroacetic acid and ammonium hydroxide. This was diluted to about 35 ml with distilled water; 10 ml of ammonium molybdate 0.2 M with respect to MoO_4^{-2} was added (0.04 M strength in reaction), and then diluted to volume with distilled water. The reaction was timed from the addition of ammonium molybdate solution, and the absorbance in this series of experiments measured on a Beckman Model B spectrophotometer at a wavelength of 400 $m\mu$.

Some of the results obtained in this comparative series of experiments are recorded in Fig. 1. The main conclusions to be noted at this stage are:

1. When sulphuric acid is used, maximum absorbance is attained within 10 min over the pH range 0.75 to 4.25 (within 2 min at pH 1.75 to 2.25), thereafter decreasing to the same constant value over a period of 48 h, the decrease being most rapid in the more acid range. Above pH 4.75 values increase with time, very slowly above pH 5.0; below pH 0.75 absorbance either continues to increase up to 5 h and then decreases or, at pH 0.5, continues to increase with time.

The maximum values (corresponding to the formation of predominantly β -silicomolybdic acid) occur between pH 1.0 and 2.5, but with no well defined plateau of constant values; the low plateau observed after 10-min reaction time between pH 3.75 and 4.25 probably corresponds to the formation of dominant α -silicomolybdic acid, all higher values at higher acidities tending to decrease to this level, and all lower values at lower acidities tending to increase to this level.

2. Whereas the same general pattern is discernible when monochloroacetic acid is used, there is one important difference: the whole curve is shifted towards lower pH values compared with that obtained with sulphuric acid. Moreover, the rates of formation and decay of the complexes at any particular pH differ compared with the sulphuric acid reaction.

Clearly, pH is not entirely responsible in determining the formation of the silicomolybdate complexes; the acidifying agency itself appears to affect the rate of formation of the complexes, and the relative amounts of α - and β -silicomolybdic acid at any particular pH. The remainder of the experiments described and reported below were aimed at understanding better the factors controlling the formation of these complexes. All these subsequent experiments were performed with a Beckman Model DU spectrophotometer at a wavelength of 400 $m\mu$ and constant slit width of 0.04 $m\mu$.

Variation in absorbance depending upon concentration of ammonium molybdate, and pH of stock solution of ammonium molybdate

The effect upon the rate of formation and the relative amounts of α - and β -silicomolybdic acid over a pH range of 0.5 to about 5.0 caused by variation in the concentration of molybdate and the pH of the stock solution, was investigated for concentrations of ammonium molybdate from 0.01 M to 0.1 M with respect to MoO_4^{-2} in the reaction. It was found that unless the pH of the stock solution was kept above about 7.0, reproducible results were not obtained using ammonium molybdate solutions more than 12 h old. Solutions which had a pH of greater than 7.0 (pH adjusted with NaOH) gave reproducible results for at least one week after preparation.

Partial results of these determinations are shown in Fig. 2 from which it is clear that the most useful concentration is 0.06 M with respect to MoO_4^{-2} in reaction, the stock solution being at a pH of about 7.0. With this concentration of ammonium molybdate, complete reaction within two minutes to give the same absorbance value

occurs over the pH range of 1.1 to 1.6 (corresponding to the addition of 5.0 to 2.7 equiv. of acid per mole MoO_4^{2-}), whilst complete reaction to give a constant absorbance in 10 min occurs in the pH range 0.9 to 1.6 (corresponding to 6.7 to 2.7 equiv. of acid per mole MoO_4^{2-}). Variation in concentration of molybdate when considered in relation to pH exerts a considerable effect upon the absolute value of absorbance attained in a given time and, whereas the pH of the stock solution affects the absolute value, its greatest effect is upon the rate of formation of the silicomolybdate complexes.

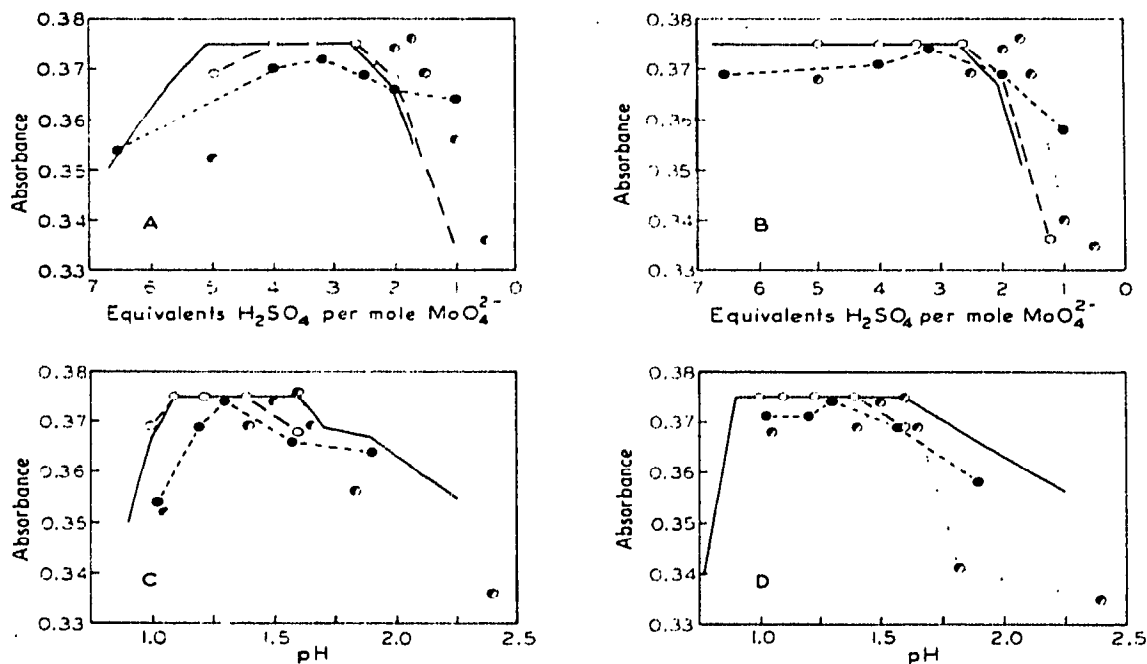


Fig. 2. Comparison of the variation in absorbance of silicomolybdate solutions with acidity and time due to variation in the concentration of molybdate. Sulphuric acid is used to acidify, and the results are shown as a function of both pH and equivalents of acid per mole MoO_4^{2-} . —○— 0.06 M with respect to MoO_4^{2-} in reaction. Stock solution 0.3 M, pH 7.3; ○—○ 0.06 M with respect to MoO_4^{2-} in reaction. Stock solution 0.3 M, pH 6.2; ●.....● 0.04 M with respect to MoO_4^{2-} in reaction. Stock solution 0.2 M, pH 5.2; ●---● 0.03 M with respect to MoO_4^{2-} in reaction. Stock solution 0.5 M, pH 5.2. A, absorbance measured 2 min after start of reaction. B, absorbance measured 10 min after start of reaction. C, absorbance measured 2 min after start of reaction. D, absorbance measured 10 min after start of reaction.

Variation in absorbance due to sulphuric and hydrochloric acids

Two series of experiments over a pH range of 0.5 to 5.5 were run using 1 N H_2SO_4 and 1 N HCl respectively. In such series various strengths ammonium molybdate were used, and results for 0.3 M stock solution at pH 7.3 (0.06 M in reaction with respect to MoO_4^{2-}) are recorded in Figs. 3 and 4. In Fig. 3, where absorbance is plotted against pH, it is seen that the absorbance at any pH is greater for the HCl series compared with the H_2SO_4 series, a difference which becomes more prominent below a pH of 1.0. Although the pattern of the curve for H_2SO_4 and HCl is the same, the plateau of high values for HCl is displaced to the acid side compared with H_2SO_4 .

In Fig. 4 the absorbance is plotted against equiv. of acid per mole MoO_4^{2-} . The absorbance after 10 min shows no significant difference between HCl and H_2SO_4 until more than 1.5 equiv. acid per mole MoO_4^{2-} have been added; at higher concentrations of acid the absorbance for HCl attains a constant greater value than for corresponding concentrations of H_2SO_4 . The absorbance values for HCl in the plateau area show a small variation, and are not as consistent as those obtained with H_2SO_4 .

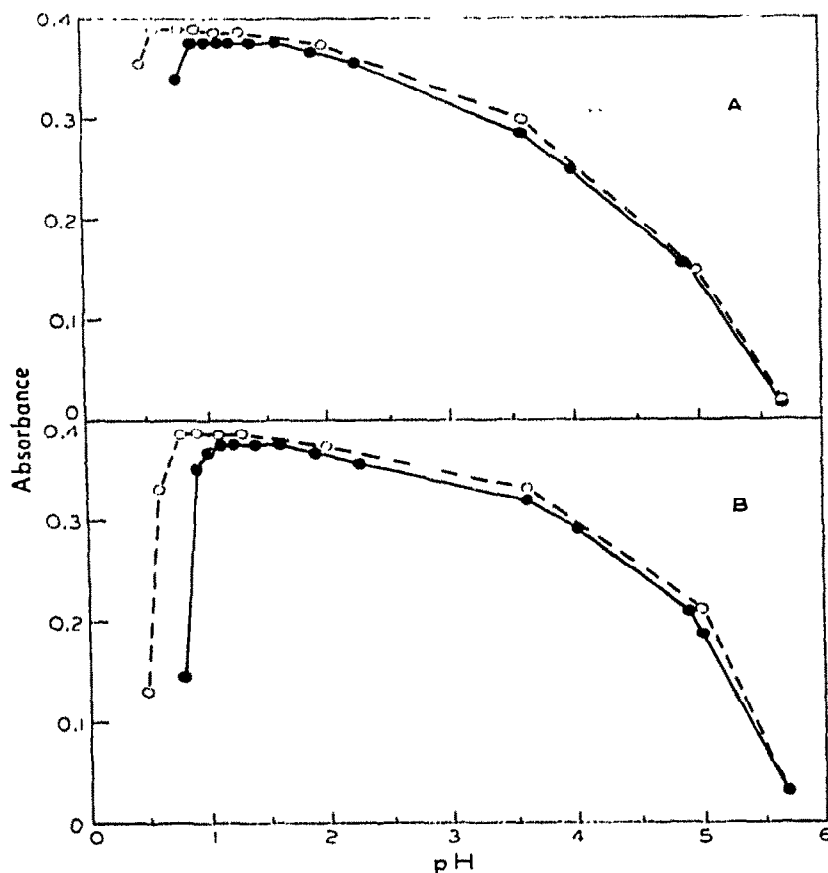


Fig. 3. Comparison of the variation in absorbance of silicomolybdate solutions due to sulphuric and hydrochloric acid as acidifying agencies. Absorbance shown as a function of pH. A, absorbance measured 10 min after start of reaction. B, absorbance measured 2 min after start of reaction.
● — ● acidified with H_2SO_4 ; ○ - - - ○ acidified with HCl.

DISCUSSION

Variation in pH is clearly an important, but not an exclusively responsible, factor in the variation in the development of yellow silicomolybdate complexes. This variation is due to the effect of pH upon the state of the molybdate ions and, as pointed out by MULLIN AND RILEY¹³, the rate of formation of silicomolybdate is dependent upon the degree of polymerization of molybdate from which it is formed.

RINGBOM *et al.*¹¹ quoted LINDQVIST¹⁴ as saying that MoO_4^{2-} ions are stable at pH greater than 6.5, that around pH 4.5 paramolybdate ions ($\text{Mo}_7\text{O}_{24}^{-6}$) are formed which are transformed into octomolybdate ions ($\text{Mo}_8\text{O}_{26}^{-4}$) at a pH of 1.5 to 2.9. RINGBOM

*et al.*¹¹ believed that the low-absorbance α -acid is formed from the paramolybdate ion, and the high-absorbance β -acid from the octomolybdate ion. STRICKLAND¹⁰ suggested that concentration must be considered together with acidity: thus, at suitable

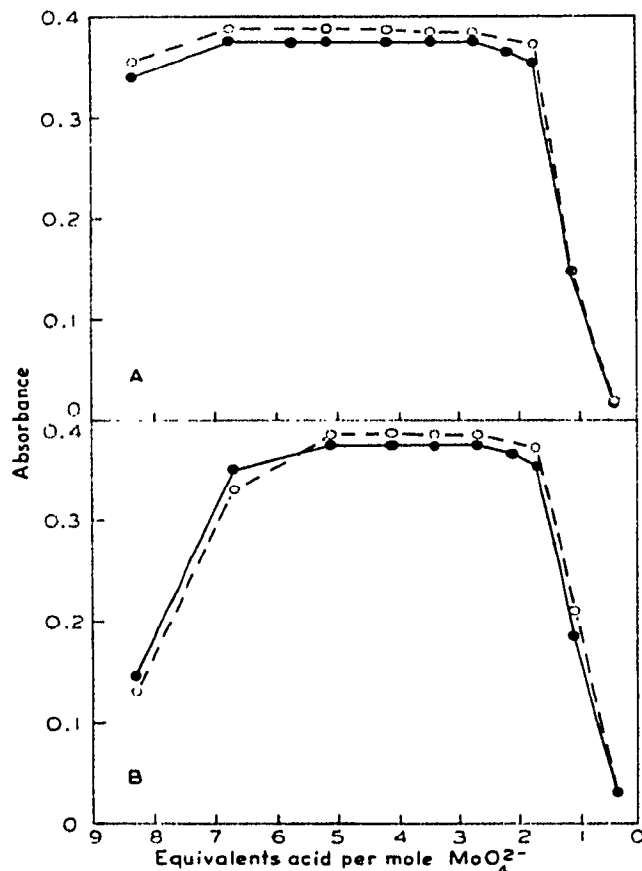
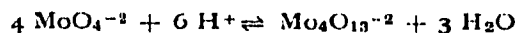


Fig. 4. Comparison of the variation in absorbance of silicomolybdate solutions due to sulphuric and hydrochloric acid as acidifying agencies. Absorbance shown as a function of equivalents acid per mole MoO_4^{2-} . A, absorbance measured 10 min after start of reaction. B, absorbance measured 2 min after start of reaction. \circ — \circ H_2SO_4 ; \bullet — \bullet HCl .

acidities, and solutions more dilute than $0.01\text{ }M$ with respect to MoO_4^{2-} ,



whilst at higher concentrations,



In solutions more concentrated than 0.05 – $0.1\text{ }M$, and acidified with 1 – 1.5 equiv. acid,



STRICKLAND¹⁰ correlated the β -forming species with the meta ion, $\text{Mo}_4\text{O}_{13}^{2-}$, but failed to identify the α -forming species. Therefore, the amount of β -silicomolybdic acid formed, and the rate of formation, will depend upon the amount of β -forming species in the molybdate added, and the rate of change of the molybdate at the

dilution and acidity in the reaction vessel. This is further complicated by the spontaneous and irreversible change of β -silicomolybdic acid to α -silicomolybdic acid. Thus, if the molybdate is added in such a form and under such conditions that its change to the β -forming species is very slow, then the earlier-formed β -acid will have changed to the α -acid before all the silica has reacted. This will give low results if the β -acid is being measured; they will be even lower if some α -forming species is initially present in the molybdate added.

Obviously, if the solution chemistry of molybdic acid, and the ion-form of molybdate which reacts with silica to form the various silicomolybdic acids, were completely understood, the molybdate should be added in the form, and into the correct conditions, to yield the form of silicomolybdic acid desired. Inasmuch as solutions of ammonium molybdate made up at a pH of less than 6.5 polymerize with time, and because the chemistry of molybdate in solution is so imperfectly known, it is analytically safer to add molybdate in the form of the simple MoO_4^{-2} ion in solutions of pH greater than 6.5. To allow any latitude in the aliquot of silica solution used the quantity of molybdate added must be comparatively small, and consequently there will be considerable change in the concentration in the reaction vessel compared with the stock solution. For example, adding ammonium molybdate solution at its natural pH of about 5.2 and in such amounts that its concentration in the reaction is 0.03 M with respect to MoO_4^{-2} , considerable variation in absorbance was found depending upon whether the solution was diluted to volume (less volume of ammonium molybdate) before addition of molybdate, or all dilution reserved until after addition of molybdate. When using ammonium molybdate from stock solutions at pH 7.3 and in such quantities as to give a concentration of 0.06 M in the reaction, the broad pH zone over which the same constant values are obtained (Fig. 2) results in there being no difference in absorbance due to differences in initial and final acidity in the reaction vessel.

The much reduced rate of reaction between silica and molybdate solutions at acidities greater than pH 1.0 was suggested by MULLIN AND RILEY¹³ to be due to polymerization of silicic acid. This is demonstrably not so in solutions less concentrated than about 100 p.p.m. SiO_2 . An impressive number of workers^{1,9,15-17} have shown that monosilicic acid solutions are quite stable up to concentrations of 100 to 150 p.p.m. irrespective of pH. To prove the point, a solution containing 1 mg monosilicic acid at a concentration of about 50 p.p.m. was allowed to stand at a pH of 0.3 for 24 h. This solution was then brought up to a pH of 1.5 and ammonium molybdate added. The absorbance was found to be the same as when the same total reagents were used but the silica added at a pH of 1.5. For these reasons it is believed that STRICKLAND'S¹⁰ contention that non-reaction or very slow reaction at high acidities is due to the presence of a non-reactive form of molybdate is correct. STRICKLAND¹⁰ postulated that at very high acidities molybdate is present in a γ -form, probably as the cationic ion MoO_2^{+2} formed from β -molybdate. The γ -molybdate is said to be completely unreactive towards silica, but the slow reaction noted at high acidities is due to a transient stability of the β -form before its conversion to γ -molybdate. It may be noted that polymers of silica smaller than 20 $m\mu$ are depolymerized to the monomeric form in the presence of ammonium molybdate¹⁸.

The effect of sulphate ion, as pointed out by STRICKLAND¹⁰ is to cause the development of more α -acid (*i.e.* lower absorbance) than a corresponding amount of chloride ion (Figs. 3 and 4). The stability of β -acid seems to be greater, however, when H_2SO_4

is used as the acidifying agent; the maximum color development (in the range 2.7 to 5.0 equiv. acid per mole MoO_4^{-2}) is attained within 2 min and remains stable for at least 20 min. Absorbance obtained with HCl shows a slight variation after 2 min in the same acidity range and, unlike H_2SO_4 , is not exactly the same value over this range. Clearly, although H_2SO_4 causes a small reduction in absorbance compared with HCl due to the formation of α -acid, the sulphate ion appears to stabilize the β -acid formed.

Increase in temperature accelerates the change β - to α -acid¹⁰, and boiling temperatures were utilized in the analytical method of RINGBOM *et al.*¹¹ to ensure the rapid and complete formation of α -silicomolybdic acid. There is also a positive temperature-absorbance coefficient for both α -acid¹¹ and β -acid¹⁰. A high temperature factor of 0.004 absorbance units per degree centigrade was reported for α -acid. The maximum variation found by the writer in admittedly few experiments was 0.001 absorbance units per degree centigrade up to 35°; above 35° the positive variation was offset by the formation of significant amounts of α -acid.

ANALYTICAL CONSIDERATIONS

In formulating a method for the determination of silica, it is desirable that conditions be such that the color is reproducible, stable over a reasonable period of time, relatively insensitive to pH variation, in some cases capable of measuring total and soluble silica, and be as rapid as possible.

It cannot be denied that the observation by RINGBOM *et al.*¹¹ that the best analytical conditions are obtained by the development of the stable α -silicomolybdic acid is most logical. The necessity of boiling the solutions to promote complete formation of the α -acid is, however, time-consuming, and leads to complications when it is desired to estimate the amount of monosilicic acid as well as total silica in aqueous samples. Moreover, the sensitivity of the test using the α -acid is considerably reduced compared with the β -acid.

It is believed that the present work completely vindicates STRICKLAND's¹⁰ suggestions that to ensure development of β -acid it is necessary that the concentration of molybdate be such that $[\text{Mo}] = 0.05$ after the silica has combined, and that there should be 3 to 5 gram equiv. of hydrogen ion per gram ion MoO_4^{-2} . Whereas most published analytical techniques have strived after the formation of the β -acid, the lack of concordance between authors and dissatisfaction with the methods (as evidenced by the large number of published works on molybdate methods for determining SiO_2) is due to lack of appreciation of the fact that two forms of silicomolybdic acid exist, and insufficient precautions to ensure constant development of one of these forms. Thus, the concentration of ammonium molybdate in the reaction proposed by BUNTING¹⁰ is barely enough to react with 2 mg SiO_2 and in no way constitutes an excess as defined by STRICKLAND¹⁰; the practice of strongly acidifying the ammonium molybdate stock solution allows uncontrolled and unknown polymerization to take place. Methods which advise waiting "about an hour" for the full development of color are clearly open to great variation, whilst heating the sample under conditions of dominant β -acid formation can only lead to the formation of variable amounts of α -acid.

The knowledge that ammonium molybdate reacts rapidly only with monosilicic acid, and the fact that monosilicic acid present in concentrations much above 100 p.p.m.

will polymerize makes the initial treatment of solid samples — and aqueous samples of high silica concentration — of critical importance. It is, therefore, necessary to use weights and volumes such that the concentration of silica in the final sample solution should not be greater than 100 p.p.m. CARRERO AND RAMALLO²⁰ stated that quartz could be accurately brought into solution at reasonable temperatures and within a reasonable time only with NaOH; the writer has found that Na₂CO₃ fusions are liable to give low results, and that solid NaOH should be used for both solid and high-silica aqueous samples.

The interference of other ions has not been investigated during the present study. MULLIN AND RILEY¹³ reported upon the interference of a comprehensive list of cations and anions. The most important source of interference likely to be encountered in most geological work is from iron and phosphorous. MULLIN AND RILEY¹³ found that by reducing iron with hydroxylamine hydrochloride, 0.2 p.p.m. Si can be determined in the presence of 100 p.p.m. ferric iron with an error of less than 1%; suppression of phosphorous was achieved by addition of oxalic acid after a method by SCHWARTZ²¹, allowing 0.2 p.p.m. Si to be determined in the presence of 5 p.p.m. of phosphate with no error. RINGBOM *et al.*¹¹ recommended the use of EDTA to avoid the formation of precipitates during the dissolution of silicate melts, and although the iron-EDTA complex has a small absorbance at 400 m μ , this can be corrected by a blank; tartaric acid was found to be the best agent to mask phosphorous, but the masking was apparently not complete at 390 m μ . LINDSAY AND BIELENBERG²² used sodium citrate to destroy the phosphomolybdate complex, whilst BUNTING¹⁹ employed tartaric acid for the dual purpose of suppressing both iron and phosphorous.

The employment of the reduced blue silicomolybdate complex offers a number of analytical advantages — there is no temperature coefficient and it has greater sensitivity — but suffers the disadvantage of being time-consuming and not well suited if it is desired to estimate the proportion of monosilicic acid as well as total silica in aqueous samples. The success or failure of the reduction method depends upon the same factors as when employing the unreduced complex, although the reducing agent may be of importance in some cases¹³. As determined by STRICKLAND¹⁰, formation of a mixture of α - and β -silicomolybdic acids either initially or by rapid change of β - to α -acid, will give on reduction a mixture of α -silicomolybdous (greenish-blue) and β -silicomolybdous (royal blue) acid which have markedly different absorbance at wavelengths used, *i.e.* above 625 m μ .

Method adopted

Preparation of sample. Solid samples should be fused with solid NaOH (in the ratio of about 3 g NaOH to 0.1 g sample) in nickel crucibles for at least 10 min. The melt is leached into a plastic beaker and acidified with sufficient 1 N sulphuric acid to give a pH of about 1.5 to the final solution. The total dilution will depend upon the amount of silica anticipated in the sample; the dilution may be achieved by diluting to volume in 500- or 1,000-ml volumetric flasks or, for greater accuracy, by diluting by weight in the plastic beaker. It must be stressed that the sample solution must not be strongly alkaline when added to glassware, for silica will be dissolved leading to erroneous results.

When it is desired to determine total silica in aqueous samples, a suitable aliquot should be boiled with solid NaOH in a nickel beaker, and then diluted as above. No treatment is necessary for determination of soluble silica.

Procedure. A suitable aliquot of sample solution is added to a 50-ml volumetric flask, acidified with 10 ml 1 *N* H₂SO₄, and followed by 10 ml of 0.3 *M* (with respect to MoO₄⁻²) ammonium molybdate. The latter solution is prepared by dissolving 52.97 g of crystalline (NH₄)₆Mo₇O₂₄·4 H₂O in one litre of water with sufficient sodium hydroxide to give a pH of not less than 7.0. The sample is diluted to 50 ml with distilled water. The absorbance is measured at 400 mμ (at a slit width of 0.04 mμ when using a Beckman Model DU spectrophotometer). The reaction with monosilicic acid is complete within 2 min and if the proportion of monosilicic acid is to be determined in an aqueous sample, the reading should be taken at 2 min; if total silica is being determined (which, of course, will be present as monosilicic acid after sample treatment) the reading should be taken not sooner than 2 min nor later than 10 min after addition of ammonium molybdate.

Calculation of the silica content is made by reference to a standard curve. Standard silica solutions may be prepared either directly by dissolving sodium metasilicate (Na₂SiO₃·9 H₂O) in distilled water acidified with H₂SO₄ so that the final pH is about 1.5 (about 60 ml 1 *N* H₂SO₄ per litre) or by fusion of standard feldspar or pure quartz in the same manner as outlined for preparing solid samples for silica determinations. The concentration of the stock solution should not be greater than 100 p.p.m. SiO₂; 50 p.p.m. SiO₂ was found to be suitable. Aliquots of the standard solution are used to prepare a standard curve for concentrations up to about 2 mg SiO₂ per 50 ml. It is important that the standard determinations should be made with the same reagents present in the same amounts as the unknown samples.

Treatment of glassware. Dirty glassware should be thoroughly cleaned with chromic acid cleaning solution, followed by washing, and then a further cleaning with 1 : 1 HCl, and a final wash with distilled water. If the glassware is regularly cleaned, it is sufficient to wash with 1 : 1 HCl. The writer confirmed the observation by MULLIN AND RILEY¹³ that if glassware is allowed to dry, even after the most stringent washing, it has an appreciable solubility under the conditions of the test. It was found convenient to leave the 50-ml volumetric flasks standing in an acid-bath containing 1 : 1 HCl, and wash well with distilled water just before use.

Replicate determinations with a standard silica solution showed a maximum standard deviation of 0.002 absorbance units in the range 0.1 to 1.0 mg silica per 50 ml. Maximum deviation occurred in the range 0.1 to 0.2 and again in the range 0.7 to 1.0 mg SiO₂ per 50 ml. The higher deviation in the lower range is attributed to pipetting error, whilst in the higher range it is probably due to lack of instrument-reading sensitivity. These determinations were carried out by the method outlined above with no special temperature control, and the standard deviation found does not include errors due to weighing or diluting of the sample; nevertheless, it is believed that it represents an adequate degree of accuracy.

ACKNOWLEDGEMENTS

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SUMMARY

The development of rapid colorimetric analytical techniques for silicates has catalysed many fundamental research programs in the geological sciences. Despite a multitude of papers on the silicomolybdate colorimetric technique for the analysis of silica which appear in the journals of nearly all sciences, it was found extremely difficult to adapt any published method for a particular purpose, and obtain reliable results. This is due to a lack of appreciation of the factors which control the silicomolybdate reaction. Data are given which indicate that the major factors are the polymer species of molybdate, which is controlled largely by the pH of molybdate stock solution; the concentration of molybdate; the ratio of acid to molybdate in reaction; and the type of acid used in the reaction. The effect of these variables is outlined, and an analytical procedure for both "soluble" and total silica outlined.

RÉSUMÉ

Une étude critique a été effectuée au sujet du dosage colorimétrique de la silice sous forme de silicomolybdate. Divers facteurs ont été examinés et la méthode, finalement adoptée, pour le dosage de la silice "soluble" et de la silice totale est décrite.

ZUSAMMENFASSUNG

Beschreibung einer kritischen Untersuchung über die colorimetrische Bestimmung von Kieselsäure als Silikomolybdat. Unter Berücksichtigung des Einflusses der verschiedenen Faktoren (pH, Konzentration etc.) wird ein Verfahren zur Bestimmung von löslicher und Gesamtkieselsäure angegeben.

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