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Studies in the Determination of Silica

III. Interference from Aluminum, Iron and Fluorine in the Spectrophotometric Determination of Silica

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Experiments with the effects of aluminum, ferric iron and sodium fluoride on the spectrophotometric silica determination are described. In the presence of aluminum the lower limit for the molybdate concentration is higher than that found for solutions containing only silica, sodium molybdate and acid. Sodium fluoride has qualitatively the same effect as aluminum. In connection with the work of Langmyhr and Graff [1] some experiments with solutions containing aluminum and sodium fluoride have also been made, which show that the pH must sometimes be chosen lower than recommended by them. In the case of iron only small amounts may be present. Iron interference has been eliminated by extraction of the iron-acetylacetone complex with carbon tetrachloride.

Ferric iron and aluminium react in water solutions with molybdate ions to form 2-heteropoly-12-molybdate ions and salts [2]. The presence of Fe(III) and Al(III) in solutions in which silica is to be determined spectrophotometrically as α-silicomolybdate may therefore have the effect of diminishing the amount of molybdate available for silicomolybdate formation. Another source of error which must be investigated is that an iron compound with molybdate may precipitate under certain conditions, removing some silicomolybdate from solution as a coprecipitate. Ferric molybdate solutions are also yellow in color at low pH values, causing high blanks. King *et al.*[3] found that small amounts of iron did not interfere with their molybdenum blue method.

When fluoride is present at least three specific effects should be considered: (1) glass vessels are attacked at low pH, (2) fluoride ions (hydrofluoric acid) may react with molybdate ions and/or (3) with silicic acid. Langmyhr and Graff [1] added aluminium to eliminate interference from fluoride in the determination of silica in hydrofluoric acid.

1. EXPERIMENTAL DETAILS

Extinction measurements were made as earlier described [4]. The temperature was 20.0° in all cases. The wavelength was 400 mμ.

pH measurements were in general carried out using a calomel reference electrode with asbestos fibre in the liquid junction. This electrode could not be used in solutions containing large amounts of aluminum chloride. An electrode with an open, bent up tip was used in such cases.

The chemicals used were of analytical grade. Acetylacetone was distilled once using a small Vigreux column.

Care must be taken that solutions containing fluoride do not remain in contact with glass long enough to dissolve measurable amounts of silica from the glass. At room temperature it is possible to handle solutions 0.1 M in NaF and 0.2 M in HCl in measuring flasks if dilution and mixing is done quickly.

If not otherwise stated, the following procedure was used in the experiments which are described later.

The silica solution was mixed with solutions of the interfering element in a polythene beaker, the pH was adjusted to the desired value and sodium molybdate solution having about the same pH was added. The pH was once more adjusted and the contents of the beaker transferred to a polythene bottle, which was placed on the steam bath. A longer heating time than that recommended earlier [4] was required with solutions containing fluoride or aluminum: 6 hours have always been sufficient. When equilibrium was reached the bottles were placed in a thermostat (20.0°C) and the solutions diluted to volume in measuring flasks before the extinction measurements

2. INTERFERENCE FROM SODIUM FLUORIDE

The ionic and molecular species that exist in aqueous solutions of sodium fluoride are determined by the following equilibria:

$$HF = H^+ + F^-$$
$$HF + F^- = HF_2^-$$

In 0.53 M KNO_3 solutions the equilibrium constants have been reported to be $10^{-2.91}$ and $10^{-0.56}$, respectively [5]. In the pH interval 1.0—4.0 the concentration of the undissociated hydrofluoric acid varies considerably with pH.

Preliminary experiments indicated that the presence of sodium fluoride increased the minimum concentration of molybdate required to obtain the full silicomolybdate color. This is shown in the following experiment, which is quite analogous to the one referred to on page 500, section 3.4 in the first paper in this series [4].

The standard procedure described in section 1 was applied. The final solutions were 0.114×10^{-3} M in Si * and 0.02 M in NaF: pH was adjusted with HCl to 3.5 and 1.5 in the solutions placed on the steam bath. The volume was then about 45 ml and the final volume was 50 ml.

In Fig. 1 the results are shown together with the curve from Fig. 5 in the previous paper [4]. The effect of decreasing the pH is to increase the effective molybdate concentration. If, however, a comparatively large excess of sodium molybdate is used, the pH interval for complete silico-molybdate formation is about the same as that obtained earlier when no fluoride was added. This is demonstrated in the following experiment.

* In the previous paper [4] sections 3.2, 3.3 and 3.4, the silica concentration is incorrectly given as 0.144×10^{-3} M in Si: the correct value is 0.114×10^{-3} M in Si.

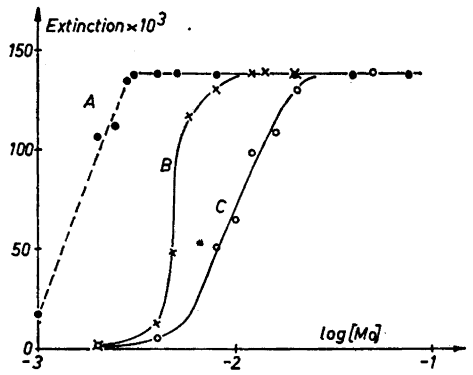

Fig. 1. Extinction as a function of the molybdate concentration for solutions containing sodium fluoride.
Curve A: 0.114×10^{-3} M Si, pH 2.0 with HCl.
Curve B: 0.114×10^{-3} M Si, 0.02 M NaF, pH 1.5 with HCl.
Curve C: » » » » » » » 3.5 » »

The standard procedure was applied. The final solutions were 0.117×10^{-3} M in Si, 0.02 M in NaF and 0.08 M in Na_2MoO_4. pH was varied between 1.0 and 4.0 by adding HCl.

The results of this experiment are given in Table 1. The extinction of blank solutions varies strongly at low pH values. Such a variation is not observed in solutions containing only silica, sodium molybdate and, *e.g.*, hydrochloric acid. Some experiments made at pH 1.0 resulted in the formation of a white precipitate: extinctions of such solutions were too low.

Langmyhr and Graff [1] have studied the behavior of solutions containing more fluoride than in the cases here treated. They show that the interfering action of fluoride can be eliminated if aluminium is added. Some experiments related to their paper are described in section 3.2.

Table 1. Extinction of silicomolybdate solutions containing sodium fluoride as a function of pH.

pH	Extinction of blank solution	Net extinction of silica solution
1.0	0.029	0.122 *
1.5	19	143
2.0	14	142
2.5	7	144
3.0	6	144
3.5	6	142
4.0	6	144

* Remark: Precipitate formed.

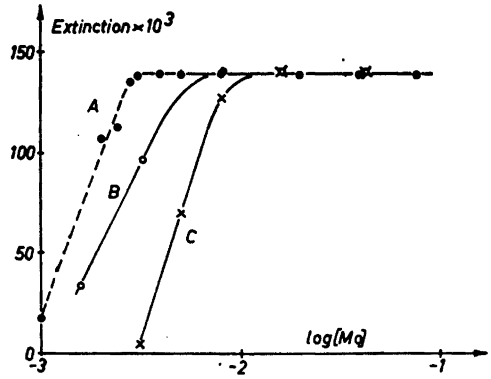

Fig. 2. Extintion as a function of the molybdate concentration for solutions containing aluminum chloride.
Curve A: 0.114 × 10^{-3} M Si, pH 2.0 with HCl.
Curve B: » » » 1.2 × 10^{-3} M Al.
Curve C: » » » 6.0 × 10^{-3} M Al.

3. INTERFERENCE FROM ALUMINUM

3.1. The effect of aluminum on the lower limit of sodium molybdate concentration.

Using the standard procedure solutions with two different aluminum concentrations were prepared. The final solutions were 0.114 × 10^{-3} M in Si, 0.0012 or 0.006 M in $AlCl_3$ and with varying sodium molybdate concentration. The pH was 2.0.

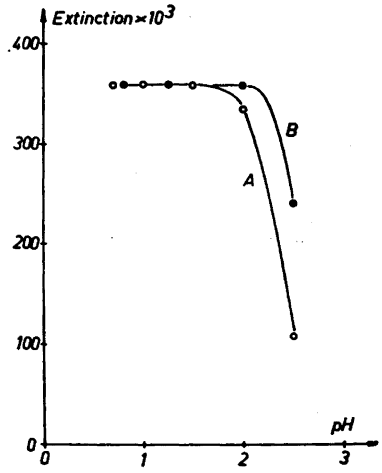

Fig. 3. Extinction as a function of pH for solutions containing aluminum chloride at two different sodium molybdate concentrations.
Curve A: 0.294 × 10^{-3} M Si, 0.1 M $AlCl_3$, 0.04 M Na_2MoO_4.
Curve B: » » » » » » 0.1 » »

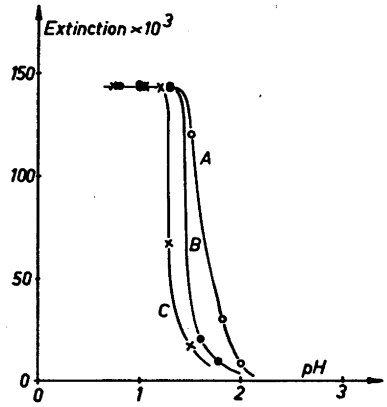

Fig. 4. Extinction as a function of pH for solutions containing sodium fluoride and large amounts of aluminum chloride.
Curve A: 0.114 × 10^{-3} M Si, 0.02 M NaF, 3.2 × 10^{-3} M Na_2MoO_4, 0.15 M Al.
Curve B: » » » » » » » » » 0.3 » »
Curve C: » » » » » » » » » 0.6 » »

Fig. 2 shows the resulting curves: the extinction has been plotted against log [Mo]. The lowest value of sodium molybdate necessary for a full development of the silicomolybdate color is higher than when no aluminum has been added.

3.2. Variation of pH in solutions of silica, sodium molybdate and aluminum chloride.

Using the standard procedure two series of solutions were prepared, which when measured in the spectrophotometer were 0.294 × 10^{-3} M in Si, 0.1 M in $AlCl_3$ and either 0.04 or 0.1 M in Na_2MoO_4. The pH was adjusted to different values with HCl.

In Fig. 3 the extinctions from the last experiments are plotted as functions of pH. The useful pH range is restricted and is a function of the molybdate concentration. It was found that a precipitate was formed when the pH was higher than about 2.5.

3.3. Experiments on the usefulness of aluminum chloride additions as a means of eliminating fluoride interference.

Langmyhr and Graff [1] were able to determine silica in hydrofluoric acid by the silicomolybdate method by adding aluminum chloride, which forms complexes with fluoride ions. They state that when their method is used the pH can be chosen anywhere in the interval 0.5—1.5. It is our experience however that the upper limit should be somewhat lower than 1.5. The following experiment is illuminating.

Using the standard procedure, series of solutions with varying pH were prepared. The aluminum concentration varied from series to series. The final solutions were 0.117 × 10^{-3} M in Si, 0.02 M in NaF and 3.2 × 10^{-3} M in Na_2MoO_4.

The curves from this experiment (Fig. 4) show that in the vicinity of pH 1.5 the extinction is a function of pH and of the aluminum concentration. It must therefore be concluded that a lower pH value than 1.5 must sometimes be chosen.

4. INTERFERENCE FROM FERRIC IRON

4.1. The presence of comparatively large amounts of iron.

If a sodium molybdate solution is mixed with a ferric chloride solution under suitable conditions, a white precipitate is formed. The possibility of determining silica spectrophotometrically in solutions in contact with such precipitates has been investigated.

The standard procedure was applied. pH was adjusted with HCl to 1.5. The final solutions were 0.3×10^{-3} M in Si, 0.05 M in Na_2MoO_4 and up to 12×10^{-3} M in $FeCl_3$. Heating on the steam bath was maintained for 3 h. The solutions were then placed in a thermostat (20.0°C) and the extinctions measured as soon as the supernatant liquids were clear. The extinction measurements were repeated several times during a period of 7 days.

The results of extinction measurements on solutions which have been allowed to stand 24 h in the thermostat are shown in Fig. 5. Measurements earlier and later indicate that the extinction of solutions in contact with precipitates is not constant but a function of time.

4.2. The presence of small amounts of iron. Variation of pH.

The investigations by Baker *et al.*[2] show that colorless complexes between ferric iron and molybdate are formed at pH values lower than about 4. It might therefore be possible to determine silica spectrophotometrically in the presence of small amounts of iron if the pH is chosen high enough.

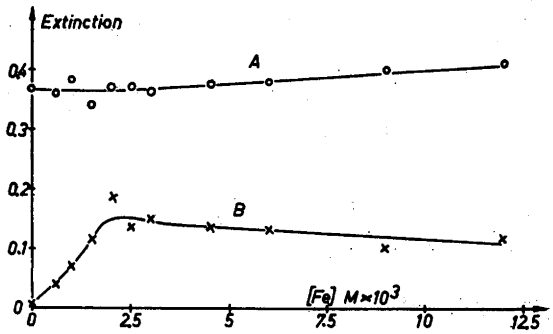

Fig. 5. Extinction in solutions containing large amounts of $FeCl_3$ as a function of the ferric iron concentration.
Curve A: 0.3×10^{-3} M Si, 0.05 M Na_2MoO_4, pH 1.5 with HCl.
Curve B: 0.05 M Na_2MoO_4, pH 1.5 with HCl.

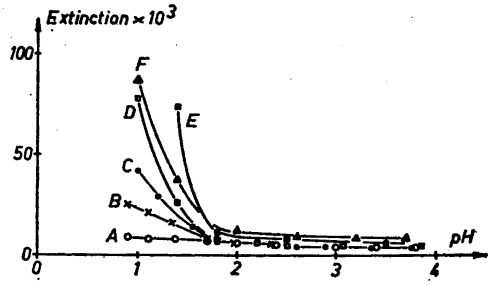

Fig. 6. Extinction of blank solutions as a function of pH at various $FeCl_3$ concentrations.
Curve A: 0.03 M Na_2MoO_4.
Curve B: » » » ,0.036 × 10^{-3} M $FeCl_3$.
Curve C: » » » ,0.09 × 10^{-3} » »
Curve D: » » » ,0.3 × 10^{-3} » »
Curve E: » » » ,0.9 × 10^{-3} » »
Curve F: 0.06 » » ,0.3 × 10^{-3} » »

Clarke [6] gave the average percent composition with respect to silicon and iron of igneous rocks as 59 % SiO_2, 3 % Fe_2O_3 and 4 % FeO. This corresponds to a Si:Fe mole ratio of roughly 10:1. If silicon is to be determined spectrophotometrically in rock analysis an iron concentration of about 0.03 × 10^{-3} M

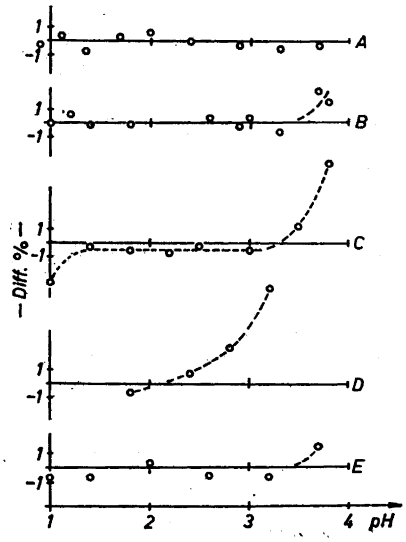

Fig. 7. Difference (in per cent of the total extinction) between measured and calculated extinction as a function of pH at various $FeCl_3$ concentrations.
Curve A: 0.3 × 10^{-3} M Si, 0.03 M Na_2MoO_4, 0.036 × 10^{-3} M $FeCl_3$
Curve B: » » » » » 0.09 × 10^{-3} » »
Curve C: » » » » » 0.3 × 10^{-3} » »
Curve D: » » » » » 0.9 × 10^{-3} » »
Curve E: » » » 0.06 » » 0.3 × 10^{-3} » »

Table 2. Extinction of silicomolybdate solutions from which iron has been removed by extraction with acetylacetone-carbon tetrachloride.

Final silica concentration (molarity)	Extinction of fluoride-free solution	Extinction of fluoride-containing solution	Calculated extinction
0.396×10^{-4}	0.048	0.049	0.048
0.396×10^{-4}	0.047	0.049	0.048
0.396×10^{-4}	0.047	0.050	0.048
0.396×10^{-3}	0.482	0.478	0.482
0.396×10^{-3}	0.484	0.484	0.482
0.396×10^{-3}	0.485	0.483	0.482

is to be expected for a silica concentration chosen to give an extinction of about 0.35.

The standard procedure was used and the final solutions were 0.3×10^{-3} M in Si, 0.03 or 0.06 M in Na_2MoO_4 and 0.036×10^{-3}, 0.09×10^{-3}, 0.3×10^{-3} or 0.9×10^{-3} M in $FeCl_3$. The pH was adjusted with HCl.

The results are shown in Figs. 6 and 7. The blank solutions containing ferric iron show a marked increase in extinction measured against water when the pH sinks below about 2. They are then strongly pH-dependent. For higher pH values the blank extinctions are low and uninfluenced by small changes in pH and ferric iron concentration. However, iron concentrations higher than about 0.3×10^{-3} M should not be used, since the results are then usually too high, especially at high pH values. At low pH values, precipitates may also be formed.

4.3. The effect of anions other than Cl^-.

If the anions SO_4^{2-}, NO_3^- and ClO_4^- are substituted for Cl^- in the experiments described above, results are similar except that precipitates formed more easily in HNO_3 and $HClO_4$ solutions, and the interfering action of small iron concentrations was more pronounced in H_2SO_4 solutions. Attempts to use F^- ions for complexing ferric ions proved unsuccessful.

5. EXTRACTION OF FERRIC IRON PRIOR TO THE SPECTROPHOTOMETRIC SILICA DETERMINATION

Several methods to extract ferric iron from aqueous solutions into organic phases using complexing substances are described in the literature [7]. In connection with the work presented here, it was important that after the extraction had been made, it should be possible to determine accurately the amount of silica in the remaining water phase, and that the amount of silica present before extraction should be the same as that present after extraction. The possibility that fluoride may be present had also to be taken into account.

In the method finally adopted, acetylacetone was used as the complexing agent and carbon tetrachloride as the extracting solvent. If no fluoride was present, extraction was made at pH 4. The separatory funnels were conditioned before extraction by soaking overnight in dilute HCl (pH 4). In this way, interference from dissolved glass was considerably reduced. When fluoride was present the extractions were carried out in platinum dishes at pH 7.5; the phases were mixed by a motordriven aluminum stirring rod. The heavy organic phase was drawn off with pipettes with long capillary tips.

The composition of the solutions which were extracted was about 0.57×10^{-3} M in Si, 8.6×10^{-3} M in $FeCl_3$ and in cases where fluoride had been added 30×10^{-3} M in NaF. 2 ml acetylacetone was added to this solution, pH was adjusted with HCl to the appropriate value and the extractions carried out.

When the iron had been removed with three extractions of the water phase (about 35 ml) using 5 ml portions of CCl_4, 0.50 g sodium carbonate was added to the remaining water phase in a platinum dish. After evaporation to dryness on the steam bath, the remaining organic compounds were destroyed by heating the dish over a Meker burner until a clear melt was formed. The contents of the dish were then dissolved in water and the amount of silica left determined spectrophotometrically.

The results from these experiments are summarized in Table 2.

I wish to thank Dr F. Nydahl, Head of the department of Analytical chemistry, for his interest in this investigation and for the facilities put at my disposal.

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