June, 1981] © *1981 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, ***54***, *1889—1890 (1981)* 1889

Dual-wavelength Spectrophotometric Determination of Trace Amounts of Phosphate in the Presence of Large Amounts of Silicate Using Molybdenum Blue

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(Received September 2, 1980)

Synopsis. A method is described for the determination of trace amounts of phosphate in the presence of large amounts of silicate. It is based on the difference in the absorption spectra of molybdenum blues formed from phosphate and silicate using a dual-wavelength spectrophotometer. The difference in absorbances at 797.3 nm and 825.0 nm is proportional to phosphate concentration over the range 1.60×10^{-7} to 7.00×10^{-5} M (1 M=1 mol dm^{-3}).

The spectrophotometric determinations of phosphate based on the formations of molybdophosphoric acid and molybdenum blue have been widely used. Though many different applications of these methods have been proposed,[1] difficulties are often encountered when two or more ions which can form molybdenum blue are present simultaneously. Many studies on the separation of phosphate from silicate have been reported. Fujinaga *et al.*[2] studied a solvent extractive separation of phosphate from silicate based on the difference in the behavior of molybdophosphoric acid and molybdosilicic acid toward the mixed solvents of 1-butanol–cyclohexane–water and of 1-butanol–isobutyl methyl ketone–water. Recently, a kinetic method for the simultaneous determination of phosphate and silicate, based on the difference in the formation rate of molybdenum blue was reported.[3] This method needs a careful control of the conditions. The present authors have developed a method for the determination of trace amounts of phosphate in the presence of large amounts of silicate based on the difference in the absorption spectra of molybdenum blue formed from phosphate and silicate using a dual-wavelength spectrophotometer.

Experimental

Materials. Molybdenum(VI) solution (1.00×10^{-1} M) was prepared by dissolving 12.09 g of sodium molybdate dihydrate in 500 ml of redistilled water. Working solutions were prepared by dilution with redistilled water to the desired concentrations. Molybdenum(V) ($Mo_2O_4^{2+}$) perchlorate solution was prepared as reported in a previous paper.[4] The concentration of molybdenum(V) solution was determined spectrophotometrically using the molar extinction coefficient ($\varepsilon=103$) at 384 nm.[5] The stock solution of molybdenum(V) perchlorate was stored in a refrigerator. Before use the stock solution was diluted to each desired concentration. This molybdenum(V) solution was stable for at least two months. Phosphate solution was prepared from sodium dihydrogenphosphate dihydrate, and silicate solution by fusing pure silica with anhydrous sodium carbonate. All the other chemicals were of analytical grade.

Apparatus. A Hitachi 356 type dual-wavelength spectrophotometer was used for the measurements of difference in absorbances at two different wavelengths.[6]

General Procedure for the Determination of Phosphate. For each run, 2 ml of 1.0 M perchloric acid, 8 ml of 2.00×10^{-2} M molybdenum(VI), 6 ml of 1.60×10^{-2} M molybdenum(V) in 2.0 M perchloric acid, and 3 ml of 4.00×10^{-4} M phosphate and 5 ml of 3.34×10^{-3} M silicate solutions were pipetted into a 50-ml measuring flask. After dilution to 50 ml with redistilled water, the solution was thermostated for 20 min at 80 °C. Below 8.00×10^{-7} M phosphate, the thermostating time was 50 min at 80 °C. The difference in absorbances at 797.3 nm and 825.0 nm was measured by a dual-wavelength spectrophotometer; two wavelengths were chosen: 825.0 nm, which is the absorption maximum of the molybdenum blue from phosphate; and 797.3 nm, at which the molydenum blue from silicate gives the same molar extinction coefficient as that at 825.0 nm.

Results and Discussion

Absorption Spectra of Molybdenum Blue Formed from Phosphate and Silicate. The absorption spectra of the molybdenum blue formed from phosphate and silicate with a mixture of 1.80×10^{-3} M molybdenum(V) and 3.20×10^{-3} M molybdenum(VI) in 0.28 M perchloric acid are shown in Fig. 1; the spectrum was measured after the solution had been thermostated for 20 min at 80 °C. The absorption maximum of molybdenum blue from phosphate appears at 825 nm (curve (A)). Curve (B) is the absorption spectrum (λ_{max} 810 nm) of the molybdenum blue from silicate. The thermostating for 20 min at 80 °C provides complete formation of molybdenum blue from phosphate, but only a partial formation of molybdenum blue from silicate, because of the small rate of molybdenum blue formation. The effect of the perchloric-acid concentration on the formation of molybdenum blue from phosphate showed that the

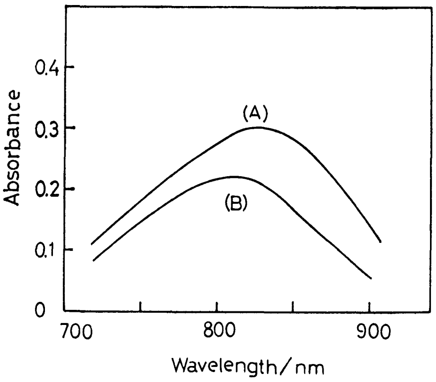

Fig. 1. The absorption spectra of molybdenum blues. (A): 1.60×10^{-5} M phosphate, (B): 2.00×10^{-4} M silicate (SiO^{2+}), both with 3.20×10^{-3} M Mo(VI), 1.80×10^{-3} M Mo(V), 0.28 M $HClO_4$. The absorption spectra (A) and (B) were measured after thermostating 20 min at 80 °C.

maximum absorbance was obtained in the range from 0.20 to 0.41 M with 2.90×10^{-5} M phosphate, 1.76×10^{-3} M molybdenum(V), and 3.20×10^{-3} M molybdenum(VI) by thermostating at 80 °C for 20 min. The rate of the formation of molybdenum blue from silicate decreases with the increase in the perchloric-acid concentration in the range from 0.25 to 5.0 M. For concentrations below 0.20 M perchloric acid, molybdenum(VI) reacts with molybdenum(V) to give isomolybdenum blue. In this work the perchloric-acid concentration of the reaction solution was adjusted to 0.28 M, and the reaction solution was thermostated for 20 min. Almost the same concentrations of molybdenum(V) and molybdenum(VI) as used previously for the determination of phosphate4) were adopted for the determination of phosphate using a dual-wavelength spectrophotometer.

Calibration Curve. The calibration curve was obtained by the general procedure for the determination of phosphate. The calibration curve is linear in the phosphate range of 1.60×10^{-5} to 7.00×10^{-5} M (0—1.0 full scale), 1.80×10^{-6}—8.00×10^{-6} M (0—0.1 full scale), and 1.60×10^{-7}—8.0×10^{-7} M (0—0.01 full scale).

Table 1. Determinations of phosphate in the presence of 3.34×10^{-4} M silicate

PO_4^{3-} added/M	PO_4^{3-} found/M	Error/%
6.3×10^{-7}	5.8×10^{-7}	−9.2
2.4×10^{-6}	2.3×10^{-6}	−4.2
6.3×10^{-6}	6.6×10^{-6}	4.8
9.8×10^{-6}	9.7×10^{-6}	−1.0
3.0×10^{-5}	2.9×10^{-5}	−3.3

[Mo(V)]$=3.20\times10^{-3}$ M, [Mo(V)]$=1.80\times10^{-3}$ M, [$HClO_4$]$=0.28$ M.

Table 1 shows the results of the determination of phosphate in the presence of 3.34×10^{-4} M silicate.

Effect of Diverse Ions. The effect of diverse ions on the determinations of phosphate was previously examined in detail.4) In the present work, these effects were not reexamined. Metal ions such as Mg^{2+}, Ca^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+}, Fe^{3+}, Al^{3+}, Cr^{3+}, and UO_2^{2+} do not interfere with the determination of phosphate, in concentrations up to *ca.* 100 molar amounts. The presence of more than 500 molar amounts of Fe^{3+} can be tolerated by adding sodium hydrogensulfite solution. The presence of an equimolar amount of As(V) interferes somewhat with the determination of phosphate.

Determination of Phosphate in the Hinuma River. One liter of the sample was evaporated to 100 ml. A 10 ml of 1.6 M HNO_3 was added to the solution, and then the solution was evaporated to 20 ml on a sand bath. After neutralization with sodium hydroxide solution and dilution to 100 ml with redistilled water the solution was filtered. The phosphate concentration was determined by the general procedure. The phosphate concentration was found to be 7.0×10^{-6} M.

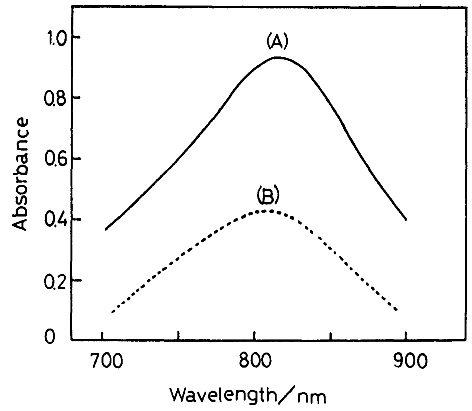

Fig. 2. The absorption spectra of molybdenum blue. (A): 12 ml of the 10-fold concentrated sample, conditions as for Fig. 1. (B): Absorption spectrum obtained by the subtraction of the spectrum of molybdenum blue obtained using the determined phosphate concentration from a curve (A).

Curve (A) in Fig. 2 is the absorption spectrum of the molybdenum blue formed by the general procedure for the color development of molybdenum blue. Curve (B) is the absorption spectrum obtained by subtraction of the absorption spectrum of the molybdenum blue prepared using the phosphate concentration determined from curve (A). The spectrum coincides with that of the molybdenum blue from silicate. A trace amount of phosphate in the Hinuma River, which contains large amounts of soluble silicate, was determined by the present method.

The method described here will be widely applicable to the determination of phosphate in samples containing silicate.

References

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