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Spectrophotometric Determination of Niobium as Reduced Molybdoniobic Acid

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▶ **The reduction product of a complex molybdoniobate is used as the basis for a spectrophotometric method for the determination of niobium(V). The effects of several variables on the color-forming reactions are described, along with the optimum conditions for formation of the blue hue. The system conforms to Beer's law in the range 0.1 to 10 p.p.m. for a 1-cm. cell. The system was applied to the determination of niobium in steel.**

BECAUSE of increasing use of niobium, especially in corrosion-resistant steels, there is a need for sensitive methods for its determination in alloys, slags, ores, and other raw materials.

Various chromogenic reagents have been used in the photometric determination of niobium, but only two references were found which reported the use of a system which the authors assume was a heteropoly complex. The species prepared by Davydov, Vaisberg, and Burkser (*4*) contained phosphorus, niobium, and molybdenum. On reduction, it formed a blue system the intensity of which was inversely proportional to the content of niobium. Later Norwitz and Codell (*9*) improved the method. This ternary system is analogous to one containing phosphorus, vanadium, and molybdenum (*7*), which is usually designated as a mixed heteropoly complex.

The existence of heteropoly species containing niobium has been postulated for some time, but the evidence is not conclusive. Smith (*13*) observed that niobic acid did not precipitate in the presence of arsenic or titanic acids. He concluded that soluble complex nioboarsenates or titanoniobates were formed. Rose (*10*) proposed a complex composition for the precipitate formed on adding a phosphate to a concentrated solution of alkali niobate. Others have suggested that niobium functions as a central atom in complexes (*2, 5, 11*). The literature revealed no reference to the actual preparation of a heteropoly complex containing niobium.

Wallace made a preliminary study of systems believed to be simple heteropoly complexes of niobium (*14*). This paper is a continuation of the earlier work, including an investigation of the analytical application of the molybdoniobate system.

EXPERIMENTAL

Apparatus. A Cary recording spectrophotometer, Model 10–11, was used, with matched quartz absorption cells 1.000 ± 0.002 cm. long. A Beckman Zeromatic meter was used for pH measurements.

Reagents. A stock solution of sodium molybdate, approximately 2%, was prepared by dissolving 20 grams of $Na_2MoO_4.2H_2O$ in water and diluting the solution to a liter.

A stock solution of niobate was prepared by fusing 0.14 gram of Nb_2O_5 with 2 grams of K_2CO_3, dissolving the melt in water, and diluting the solution to a liter. This solution, containing approximately 0.1 mg. per ml. of niobium, was standardized gravimetrically by precipitation of niobic acid and ignition to Nb_2O_5. The final solution was stored in polyethylene to prevent contamination with silica. Some niobium may be adsorbed on such a container on long storage (*3*).

A stock solution of chlorostannous acid, approximately, 10%, was prepared by dissolving 110 grams of $SnCl_2.2H_2O$ in 170 ml. of concentrated hydrochloric acid and diluting to a liter. A few pieces of mossy tin were added to the container. Dilutions of this solution were used in subsequent work.

RECOMMENDED METHOD

To obtain a system for the photometric measurement of niobium, two main chemical processes are involved: preparation of a complex, presumably a molybdoniobate; and reduction of this complex to an assumed heteropoly blue. Several variable factors affect each of these reactions.

Based partly upon previous experience with heteropoly systems, and partly upon empirical experimentation with the molybdoniobate system, the following recommended procedure was evolved.

Preparation of Calibration Curve. Prepare a calibration curve by transferring 0.0, 0.5, 1.0, 3.0, and 5.0 ml. of a solution containing 0.05 mg. per ml. of niobium to 50-ml. beakers. To each beaker add 15 ml. of 2% sodium molybdate and adjust the pH to 1.5. After 10 minutes, add, by means of a hypodermic syringe, 10 ml. of 1 to 4 sulfuric acid. After exactly 5 seconds, add, again by means of a hypodermic syringe, 2 ml. of 0.5% chlorostannous acid. Transfer the solutions to 50-ml. volumetric flasks, dilute to the mark, mix, and read the absorbance at 725 mμ exactly 4 minutes after addition of the reductant. Plot an absorbance-concentration curve.

General Procedure. Dissolve the sample containing niobium and remove any interfering ions (see Table VI) by suitable means. Concentrate the solution to 10 to 15 ml. and continue preparation of the solution and its measurement as described under Preparation of Calibration Curve. From the curve, determine the amount of niobium.

EFFECTS OF VARIABLES

In the course of developing the recommended procedure it was necessary to study the effects of variables upon the processes of complex formation and reduction. For this purpose, the following tentative method was set up. To a solution containing about 0.1 mg. of niobium, 15 ml. of 2% sodium molybdate was added, and the pH was ad-

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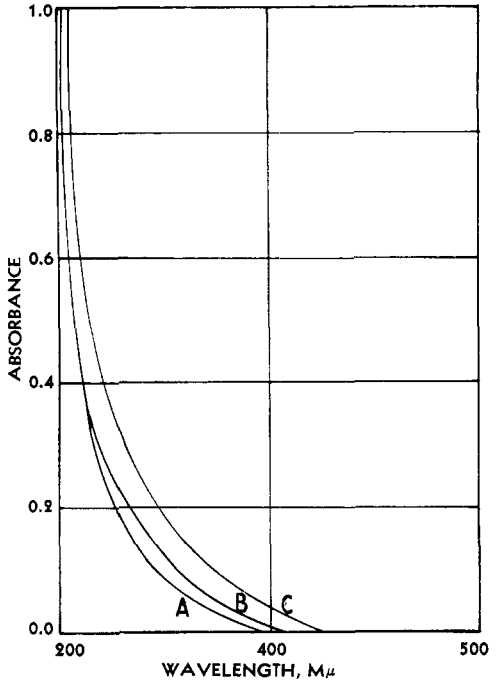

Figure 1. Absorption spectra of molybdenum-niobium complex

A. 0.0 mg. of Nb
B. 0.1 mg. of Nb
C. 0.5 mg. of Nb

justed to 1.5. After about 10 minutes, the solution was reduced with 2 ml. of 0.5% chlorostannous acid and diluted to 50 ml. This yielded a blue hue. Using this system, the problem then was to determine the effect of each variable factor and also what could be done to control them to obtain a reproducible color for measurement.

Formation of Molybdoniobate Complex. Formation of a complex of this type involves at least the following questions: What is the necessary ratio of molybdate to niobate? Is appreciable time required to form the complex? What is the optimum pH for the process? How may the excess molybdate be controlled, since it is reducible to a molybdenum blue?

Answers to these questions were sought experimentally by adapting the trial system to study the separate variables.

Evidence was sought first for a reaction between molybdate and niobate. To solutions containing 0.0, 0.1, and 0.5 mg. of niobium, 15 ml. of 2% sodium molybdate was added, the pH was adjusted to 1.5, and the volume was made up to 50 ml. The absorption spectra (Figure 1) show that there is an interaction, although the change is not great. The obvious low sensitivity precludes analytical use of this system.

In the effort to enhance the sensitivity, the system was reduced. To solutions containing 0.08 and 0.75 mg. of niobium, 15 ml. of 2% sodium molybdate was added, and the pH was adjusted. Then the solutions were reduced with 2 ml. of 0.5% chlorostannous acid, and the volume was made up to 50 ml. The absorption spectra (Figure 2) indicated reasonable sensitivity.

Effect of Molybdate Concentration. The effect of the concentration of molybdate was determined by placing 0.1 mg. of niobium in approximately 40 ml. of water, adjusting the pH to 1.5, reducing the solution with 2 ml. of 0.5% chlorostannous acid, and diluting to 50 ml. To prevent reduction of excess molybdate, the solutions were made strongly acidic with 7 ml. of 1 to 4 sulfuric acid. Under these conditions, the absorbance increased with increasing amounts of molybdate up to 15 ml. of the 2% solution. Additional molybdate had no further effect. Even with the sulfuric acid present it was necessary to apply a small blank correction in each case. This correction increased slightly with increasing concentration of molybdate.

Effect of pH. Like other heteropoly systems, the extent of complex formation, and hence the absorbance of the final solution, is a function of pH. Consequently, the optimum value was sought.

To solutions containing 0.1 mg. of niobium, 15 ml. of 2% sodium molybdate was added, and the pH was adjusted to various values. The reduction was carried out as before, and the volume was adjusted to 50 ml. The absorbance data, summarized in Table I, show that the optimum range was 1.2 to 1.6. For subsequent work, pH 1.5 was chosen.

Table I. Effect of pH on Complex Formation

(0.1 Mg. Nb/50 ml. solution)

pH	Absorbance, 725 Mμ
0.5	0.05
0.7	0.07
0.9	0.15
1.0	0.19
1.2	0.29
1.3	0.30
1.4	0.30
1.5	0.31
1.6	0.30
2.0	0.29
3.0	0.20

Effect of Time. To determine the time required for complex formation, a series of solutions, each containing 15 ml. of 2% sodium molybdate and 0.1 mg. of niobium, was prepared, and the pH was adjusted to 1.5. The solutions were allowed to stand different periods of time and then reduced, as described before. The data, summarized in Table II, show that at least 10 minutes is required for formation of the complex.

Table II. Effect of Time on Complex Formation

(0.1 Mg. Nb/50 ml. solution)

Time, Minutes	Absorbance, 725 Mμ
1	0.15
2	0.17
3	0.19
5	0.21
7	0.24
10	0.29
12	0.30

Effect of Temperature. Temperature change from 0° to 100° C. had little effect on the degree or rapidity of complex formation.

Reduction of Molybdoniobate Complex. Norwitz and Codell (*9*) reported that a slight blue hue results from the reduction of a solution containing molybdate and niobate by chlorostannous acid. The sensitivity was too low to be useful. Wallace's work showed that the process had some promise (*14*).

To isolate and optimize the effects of any variables involved in the reduction process, further work was done with the trial system, as refined up to this point.

Effect of Concentration of Sulfuric Acid. As already stated, it is necessary to have the pH about 1.5 for formation of the molybdoniobate complex, along with sufficient time for the

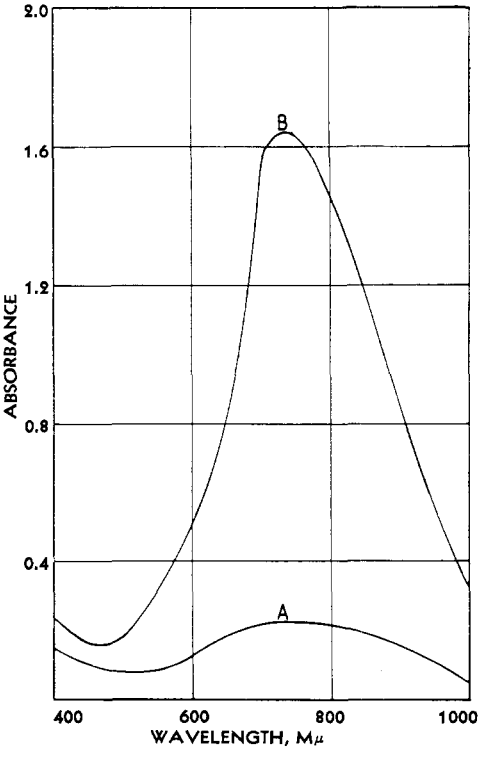

Figure 2. Absorption spectra of reduced molybdoniobate complex

A. 0.08 mg. of Nb
B. 0.75 mg. of Nb

process and an adequate excess of molybdate.

If reduction to the heteropoly blue is made at this point, both the complex and the excess molybdate will contribute. Sufficient sulfuric acid largely prevents reduction of the molybdate, but at the same time such excess acidity destroys the molybdoniobate complex, if given sufficient time. Consequently, it was necessary to determine the concentration of sulfuric acid required to eliminate the blank correction without destroying the heteropoly species before it could be reduced and measured.

To solutions containing 0.1 mg. of niobium and 15 ml. of 2% sodium molybdate, adjusted to pH 1.5, and allowed to stand 10 minutes, different amounts of 1 to 4 sulfuric acid were added from a hypodermic syringe to obtain rapid, efficient mixing. This was followed at once with 2 ml. of 0.5% chlorostannous acid, and the solution was diluted to 50 ml. and mixed. The results (Table III) show that 10 ml. of acid did not appreciably affect the sensitivity of the method, if reduction is carried out within 5 seconds after adding the acid.

Table III. Effect of Sulfuric Acid

(0.1 Mg. Nb/50 ml. solution)

Sulfuric Acid, Ml. 1 to 4	Absorbance, 725 Mμ
0.0	...
1.0	1.70
2.0	1.43
3.0	0.91
4.0	0.48
5.0	0.21
6.0	0.10
7.0	0.01
8.0	0.01
9.0	0.005
10.0	0.0

Table IV. Effect of Amount of Reductant

(0.1 Mg. Nb/50 ml. solution)

Chlorostannous Acid, Ml. 0.5%	Absorbance, 725 Mμ
0.0	0.0
0.5	0.09
1.0	0.18
2.0	0.30
5.0	0.30

Table V. Stability of Color with Time

(0.1 Mg. Nb/50 ml. solution)

Time, Minutes	Absorbance, 725 Mμ
0	0.0
1	0.20
2	0.25
3	0.28
4	0.28
5	0.28
10	0.26
15	0.24

CHOICE OF AND HANDLING REDUCTANT. As already stated, the reductant must be added as quickly as possible after the sulfuric acid. Otherwise, the complex partially decomposes before there is opportunity for its reduction. For this reason, a hypodermic syringe was used.

Several reductants were tried. Ascorbic acid or sulfuric acid–sulfite gave little blue hue. Hydrazine hydrochloride gave a weakly colored product. Ferrous ammonium sulfate or chlorostannous acid gave the best results, with the latter yielding a somewhat greater absorbance for the same concentration of niobium.

The effects of concentration of reducing agent on a system identical with that described in the previous section are summarized in Table IV. A small blank correction was necessary for the higher concentrations of reducing agent. Two milliliters of 0.5% chlorostannous acid was chosen as the most satisfactory concentration.

STABILITY OF COLOR. It was soon observed that the blue hue of the reduction product faded rapidly, a difficulty also encountered by Davydov *et al.* (*4*).

To study this variable, the blue hue was developed in a system identical with that of the previous section, and the solution was transferred rapidly to the spectrophotometer. The absorbance was measured at 725 mμ *vs.* time. The results, summarized in Table V, indicate that the absorbance should be read between 3 and 5 minutes after reduction for optimum sensitivity. An intermediate time of 4 minutes was selected for subsequent work. The stability of the reduction product was decreased in boiling water.

CONFORMITY TO BEER'S LAW. After optimization of the variables described above, varying amounts of niobium were added to otherwise identical solutions. The system followed Beer's law in the range 0.1 to 10 p.p.m. with a 1-cm. cell. A slight negative deviation occurred above 10 p.p.m.

EFFECT OF DIVERSE IONS. Effects of selected diverse ions are summarized in Table VI. A 2% error in the estimation of niobium was considered tolerable. The conditions of the recommended procedure were followed except for the addition of the diverse ions.

Ag^{+}, Ba^{+2}, Bi^{+3}, Pb^{+2}, and Sr^{+2} form insoluble precipitates under the conditions of the experiments. As^{+3}, As^{+5}, $C_2O_4^{-2}$, citrate, CN^{-}, Co^{+2}, Cr^{+3}, Cr^{+6}, F^{-}, Fe^{+2}, IO_4^{-}, PO_4^{-3}, Sb^{+3}, SCN^{-}, SeO_4^{-2}, SiO_3^{-2}, VO_3^{-}, and WO_4^{-2} interfere seriously. The other substances investigated can be tolerated to the concentrations shown.

APPLICATION OF METHOD

To check the applicability of this new method to an industrial product, NBS steel No. 123b was selected.

Transfer the sample, containing 0.01 to 0.5 mg. of niobium, to a tall form beaker, add 15 ml. of 2 to 1 hydrochloric acid, cover, and warm gently until all action ceases. Cautiously add 50 ml. of 1 to 1 nitric acid and boil until all black particles are dissolved (*8*). Add 10 ml. of 1 to 4 sulfuric acid and boil for 5 minutes. Remove any remaining residue by filtration, fuse, dissolve, and add to the beaker. Remove the iron by sulfide precipitation, and then separate the niobium (and any tantalum) by tartrate hydrolysis, and the niobium from tantalum (if necessary) by the tannin method (*12*). More recently developed separative methods may be used (*1, 6*).

Concentrate the niobium solution to 10 to 15 ml. and proceed as directed under the recommended procedure.

For the NBS sample, the certified value is 0.75%. Three determinations gave 0.72, 0.76, and 0.74%, the mean of which is 0.74. The 95% confidence limit is ±0.04%, and the standard deviation is 0.02%.

CONCLUSIONS

With meticulous attention to operating details, the new method is slightly more sensitive than the heteropoly methods previously available. One variable, the phosphate concentration, is avoided. The chief disadvantage is the possible interferences.

Perhaps the most important item about this method is the fact that pre-

Table VI. Diverse Ion Study

(0.1 Mg. Nb/50 ml. Solution)

Ion[a]	Added As	Amount Permitted, P.P.M.
Al^{+3}	$Al(NO_3)_3$	100
NH_4^{+}	NH_4NO_3	100
Br^{-}	KBr	100
B^{+3}	H_3BO_3	100
Cd^{+2}	$Cd(NO_3)_2$	100
ClO_3^{-}	$KClO_3$	100
ClO_4^{-}	$KClO_4$	100
Cu^{+2}	$CuSO_4$	40
Fe^{+3}	$Fe(NO_3)_3$	10
I^{-}	KI	100
Mg^{+2}	$MgSO_4$	100
Mn^{+2}	$MnSO_4$	100
Ni^{+2}	$NiCl_2$	100
Pd^{+2}	$PdCl_2$	100
SO_4^{-2}	Na_2SO_4	100
$S_2O_8^{-2}$	$K_2S_2O_8$	100
Zn^{+2}	$Zn(NO_3)_2$	100
Zr^{+4}	$ZrO(NO_3)_2$	25

[a] 100 p.p.m. added.

sumably a reducible heteropoly complex is formed between molybdate and niobate.

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Determination of Radioactive Calcium by Liquid Scintillation Counting

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▶ A liquid scintillation method for measuring calcium-45 is described. The method consists of precipitating calcium as the oxalate salt, converting this salt to the nitrate, and counting the nitrate in a solvent system of toluene–ethyl alcohol–ethylene glycol–nitric acid containing an organic scintillator.

ALTHOUGH there is growing literature on the use of liquid scintillation counting techniques for carbon-14 and tritium, and to a lesser extent for inorganic radioactive nuclides, there is only one published liquid scintillation method for calcium-45. Lutwak (*4*) has reported two procedures for calcium-45, including the counting as calcium 2-ethylhexanoate in a solution of toluene, and as calcium chloride (or salt) in a tertiary mixture of absolute ethyl alcohol – hydrochloric acid – toluene. Lutwak found the use of 2-ethylhexanoic acid somewhat limited in that it could not be used for urine, and that certain calcium salts required special pretreatment. He further stated that his other method using the tertiary mixture should not be used for more than 50 mg. of calcium. Our laboratory, though obtaining essentially the same results as Lutwak, did find his tertiary mixture could not be used with much more than 25 mg.

There have been other reports in which calcium-45 was counted in a liquid scintillation system, but either insufficient details were given (*1*, *7*), or the procedure is not well suited for the routine determination of this isotope (*8*).

The present work describes a method in which calcium-45 nitrate is counted in an ethylene glycol–ethyl alcohol–toluene scintillation system. The method has the advantage of a relatively low background, high efficiency usefulness over a very wide range of sample sizes, and direct applicability to calcium in any chemical form or from any biological source. Furthermore, the method is suitable for counting relatively large quantities (125 mg. of calcium) of low specific activity.

EXPERIMENTAL

Apparatus. The liquid scintillation counter is a Tri-Carb liquid scintillation spectrometer, Model 314-A (Packard Instrument Co., LaGrange, Ill.). The freezer is maintained at 0° C.

Samples are counted in 5-dram cylindrical Crystallite vials fitted with 25-mm. polyethylene snap caps (Wheaton Glass Co., Millville, N. J.).

Materials. All chemicals used were ACS reagent grade.

The scintillation system used was 1 liter of toluene containing 11.4 grams of 2,5-diphenyloxazole (DPO) (scintillation grade, Packard Instrument Co., Inc., LaGrange, Ill.), 1 liter of absolute ethyl alcohol, 250 ml. of ethylene glycol, and 12.4 ml. of nitric acid. The solution is stored in an amber bottle in the dark.

The standard used was a certified 10-μc. calcium-45 chloride solution (Nuclear-Chicago Corp., Chicago, Ill.).

Procedure. PREPARATION OF MACRO SAMPLES (bone, milk, etc.). The sample is placed in a porcelain crucible in a muffle furnace 600–800° C. for 8 or more hours. The ash is dissolved in concentrated HCl, transferred to a volumetric flask, and diluted to a known volume. An aliquot is removed, and the calcium is precipitated as the oxalate salt (*3*). The calcium oxalate is collected on a sintered glass filter crucible and washed with water. The crucible is then placed in a $1\frac{1}{2}$ inch diameter short stem glass funnel on a rack designed to support 40 funnels. Using a counting vial as the receiving vessel, a small portion of warm concentrated nitric acid is poured into the crucible. Additional warm acid is added until all the calcium oxalate is dissolved. The crucible and funnel are washed with acid. The vial is placed on a hot plate (approximately 60° to 70° C.), in a fume hood, and the acid washings are evaporated. The resulting white salt residue is heated for 15 minutes at 120° C. Twenty milliliters of the scintillation solution is added; the vial is capped and shaken until all the salt dissolves. The sample is placed in the freezer unit of the spectrometer and counted after 1 hour.

PREPARATION OF MICRO SAMPLES (serum, urine, dilute solutions, etc.). The sample is placed in a 12-ml. glass centrifuge tube, and the calcium is precipitated as the oxalate (*2*). The sample is centrifuged, the supernatant is discarded, and the precipitate is washed with water. The washed precipitate is dissolved in warm nitric acid, and the solution is transferred to a counting vial by repeated washings of the centrifuge tube with small volumes of nitric acid. The nitric acid solution is treated as described above.

RESULTS

Operating Voltage. The operating voltage was determined in the usual manner (*6*). The final operating conditions chosen were Tap 4.65 (1070 volts) with window settings of 10 to 90,