

THE DETERMINATION OF MOLYBDENUM IN
SOLUTIONS AND SOILS

by

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INTRODUCTION

Recent work in the United States, and other parts of the world, has indicated that molybdenum may be an essential or at least a beneficial element for the growth of plants. Horner et. al. (8), experimenting with artificial cultures of Azotobacter, found that 1 to 4 ppm of molybdenum increased the total nitrogen fixed approximately 6 fold. Australian investigators (10), working on the influence of molybdenum on symbiotic nitrogen fixation, found that alfalfa grown in sand cultures gave a small but significant response to molybdenum when the medium provided only 1 part of molybdenum per 80,000 parts of nitrogen fixed. Arnon and Stout (1) grew tomato seedlings in rigidly purified nutrient solutions to which the elements regarded as essential were added. The tomato plants developed deficiency symptoms in a few weeks. Additions of less than 1 ppm of molybdenum prevented the deficiency symptoms.

Excessive quantities of molybdenum are toxic to plants and animals. Arnon and Stout (1), using water culture methods, found that molybdenum concentrations of 10 to 20 ppm are usually toxic to plants. However, there is evidence that plants can withstand higher concentrations under field conditions without apparent injury to the plants themselves. Animals consuming vegetation containing excessive quantities of molybdenum develop a typical diseased condition. British investigators (4) found that the so-called "Teart disease" of livestock can be traced directly to the animal's consumption of forage containing relatively high concentrations of molybdenum. A disease similar to the "Teart disease"

found in England has developed in the San Joaquin Valley of California. Barshad (3) found that the diseased animals had in all cases consumed forage containing large quantities of molybdenum. He also found that the forage in severely affected areas was grown on soils containing from 6 to 10 ppm total molybdenum of which 3 to 6 ppm were water soluble. The disease sometimes occurred in areas where the total molybdenum content of the soil ranged from 1.5 to 4.0 ppm of which 0.8 to 2.0 ppm were water soluble. In California, the high per cent of water soluble molybdenum was associated with alkaline soils. This was attributed to the fact that molybdenum is more soluble under alkaline conditions.

Since an excess or a deficiency of molybdenum in soils may present various problems, an experiment was designed for the purpose of making a preliminary survey of some Kansas soils to determine their molybdenum content. Shortly after the work was started it became apparent that existing colorimetric methods of molybdenum determination should be modified in order to adapt their use to photoelectric instruments. A large share of the research work was devoted to this problem; therefore less time was spent on the complex problem of molybdenum determination in soils.

REVIEW OF LITERATURE

The yellow-amber color developed by molybdenum, a thiocyanate salt, and a reducing agent has been used for a number of

years for the colorimetric determination of small amounts of molybdenum. Stannous chloride has been the most common reducing agent used. Probably the greatest advantage of stannous chloride is the fact that it develops the color quickly and produces greater color intensity than other common inorganic reducing agent. Various modifications of the basic molybdenum thiocyanate-stannous chloride method have been used by investigators to determine small amounts of molybdenum in ores, rocks, soils, and plant material (2,5,12,13,14,15,18).

The complex chemistry of the molybdenum thiocyanate reduction reaction has challenged research workers and chemists. The major problems of the reaction apparently center around the development and fading of the color complex; therefore a review of literature on that subject is discussed.

The valence state of molybdenum at the time the yellow-amber color develops has been studied. Hiskey and Meloche (6,7) made a detailed study of the thiocyanate complex of molybdenum. By using known valence compounds of molybdenum, they established the fact that the yellow-amber color developed only when molybdenum was present in the quinquevalent state. These workers also found that at lower valences a greenish-blue color complex resulted. Since the yellow-amber color has been the basis for quantitative determinations of molybdenum, this established the fact that the molybdenum must be at a high valence state before reduction.

The rapid fading of the molybdenum thiocyanate color complex

has been a major problem facing investigators using stannous chloride as the reducing agent. Most investigators have prescribed definite concentrations of reagents and various other procedures for minimizing the fading of the color complex. Standards and unknowns were prepared simultaneously each time a determination was carried out in order to reduce error. Since no definite agreement existed among early investigators as to the best procedure for minimizing color fading, Hurd and Allen (9) made an analytical study of solvent extracting solutions, concentration of reagents, and other variables involved to determine the conditions which allowed the maximum color development and minimized the rate of fading of the color complex. They recommended that the concentration of hydrochloric acid be held at 5.0 per cent, potassium thiocyanate at 0.6 per cent, and stannous chloride above 0.1 per cent in the final solution to obtain the best results. Hiskey and Meloche (7) investigated the effect of various electrolytes on the stability of the color complex. They concluded that stability depended on the hydrogen ion concentration of the solution, and the dipole effect of various ions. Grimaldi and Wells (5) dispensed with extracting solutions and developed the color in a water-acetone solution using stannous chloride as the reducing agent. This procedure stabilized the color somewhat. Barshad (2) added controlled amounts of ferric iron and nitrate ion which minimized the rate of fading for a period of 30 minutes.

The basic molybdenum thiocyanate-stannous chloride method has

been used for the determination of molybdenum in soils. Two general methods of extracting molybdenum have been used. Nichols and Rogers (12) and Perrin (13) used hydrofluoric acid to volatilize the silica in soils as silicon tetra-fluoride. Robinson (14) extracted the molybdenum by means of the standard sodium carbonate fusion method for determining total amounts of elements in soils. The usual method after extraction has been to take the molybdenum up in hydrochloric acid, develop the color in the acid solution, and extract the color complex with ethyl ether. The amount of molybdenum in the soil was then determined by matching with standards of known concentrations prepared at the time each determination was carried out.

DETERMINATION OF MOLYBDENUM IN SOLUTIONS

Experimental Methods

In trying to determine the amounts of molybdenum in soils, an attempt was made to adapt the procedure outlined by Nichols and Rogers (12) to the use of an Evelyn photometer. This procedure prescribes the concentration of reagents suggested by Hurd and Allen (9) for the best results when stannous chloride is used as the reducing agent. The procedure was found to be very unsatisfactory in making a standard curve for the Evelyn photometer. The method proposed by Grimaldi and Wells (5) was also tested. This method stabilized the color to some extent. However, rapid fading of the color complex was still encountered with Grimaldi and Wells' method. Although it was possible to

standardize the procedures somewhat by establishing a fixed period of time before the readings were taken it was thought highly desirable to find a reducing agent that would give color stability over a long period of time. It was felt that color stability would certainly improve the accuracy and convenience of the determination. Therefore, a method was developed in which acetone is used directly as a reducing agent and by which color stability is obtained for a period of 48 hours. The sensitivity of the determination is also increased over the previous methods tested.

Reagents

Potassium thiocyanate (water solution). Dissolve 10 grams of potassium thiocyanate in 100 ml of distilled water.

Acetone, reagent grade.

Hydrochloric acid, sp. gr. 1.18-1.19.

Standard molybdenum solution for preparing calibration curve (1000 parts per million molybdenum). Prepare a stock solution containing 1000 ppm molybdenum by dissolving 1.8401 gm of dry ammonium molybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$) in water, and diluting to 1 liter. Prepare working standards by quantitative dilution of the stock solution.

Procedure

Evaporate or dilute the molybdenum solution to be analyzed until 20 ml of the solution contain from 5 to 1000 micrograms

of molybdenum. Place the 20 ml of solution in a 50 ml volumetric flask, and add enough hydrochloric or other nonoxidizing acid to make the final 50 ml of solution 1.2 to 2 N in respect to acid. When using water solutions of molybdenum 7 ml of hydrochloric acid are sufficient. Add 3 ml of 10 per cent potassium thiocyanate solution, and 15 ml of acetone. Place in a water bath at 60 to 70 degrees C. for at least 20 minutes. Cool, dilute to volume, and determine transmittancy in a filter or spectrophotometer at 420 millimicrons. Determine parts per million molybdenum in the solution by reference to a standard curve prepared from known standard molybdenum concentrations. A standard curve for the Evelyn photometer is shown in Fig. 1.

If it is present in high concentrations, ferric iron interferes with the molybdenum determination by the acetone reduction method. A fine precipitate was formed during the reduction process if the concentration of iron exceeded 100 ppm. When controlled amounts of ferric iron were added to solutions, a precipitate formed if the solutions contained 200 or 2,000 ppm ferric iron, but no precipitation occurred at iron concentrations of 100 ppm. If the iron concentration is less than 100 ppm, the determination can be carried out without its removal by extending the period of heating to approximately 1 hour. However, since iron has no beneficial effect on the development of the color complex by the acetone reduction method, and because a longer period of heating is required, it is recommended that the removal of iron by quantitative methods be made a standard procedure for

all determinations. Precipitation by raising the pH of the solution with ammonium hydroxide was found to be a satisfactory method for removing the iron. The iron should be removed from the solution before, the acid, thiocyanate, and acetone are added.

Since the molybdenum concentration of solutions may often be increased by evaporation and acetone reduction provides a highly sensitive method of determination, it is not recommended that the colored complex be extracted with ether or other solvents unless it is impossible to evaporate the solution sufficiently.

Discussion and Results

Table 1 compares the light transmittancies obtained with different molybdenum concentrations using various reducing agents. All the reducing agents were tried at several concentrations. NaHSO_3 , NaHSO_3 & metol, hydroxylamine hydrochloride, 1 amino-2-Naphthol-4-sulfonic acid plus Na_2SO_3 and $\text{Na}_2\text{S}_2\text{O}_5$, and camphor gave color stability but failed to give sufficient sensitivity for the determination of small amounts of molybdenum. Acetone was the only reducing agent tested that gave both color stability and sensitivity.

A comparison of the intensity of the color complex developed by different reduction methods is shown in Fig. 2, where optical density is plotted against parts per million of molybdenum. The acetone reduction method increased the sensitivity of the color complex, thus allowing a more precise determination of small amounts of molybdenum. Two ppm molybdenum, for example, produced

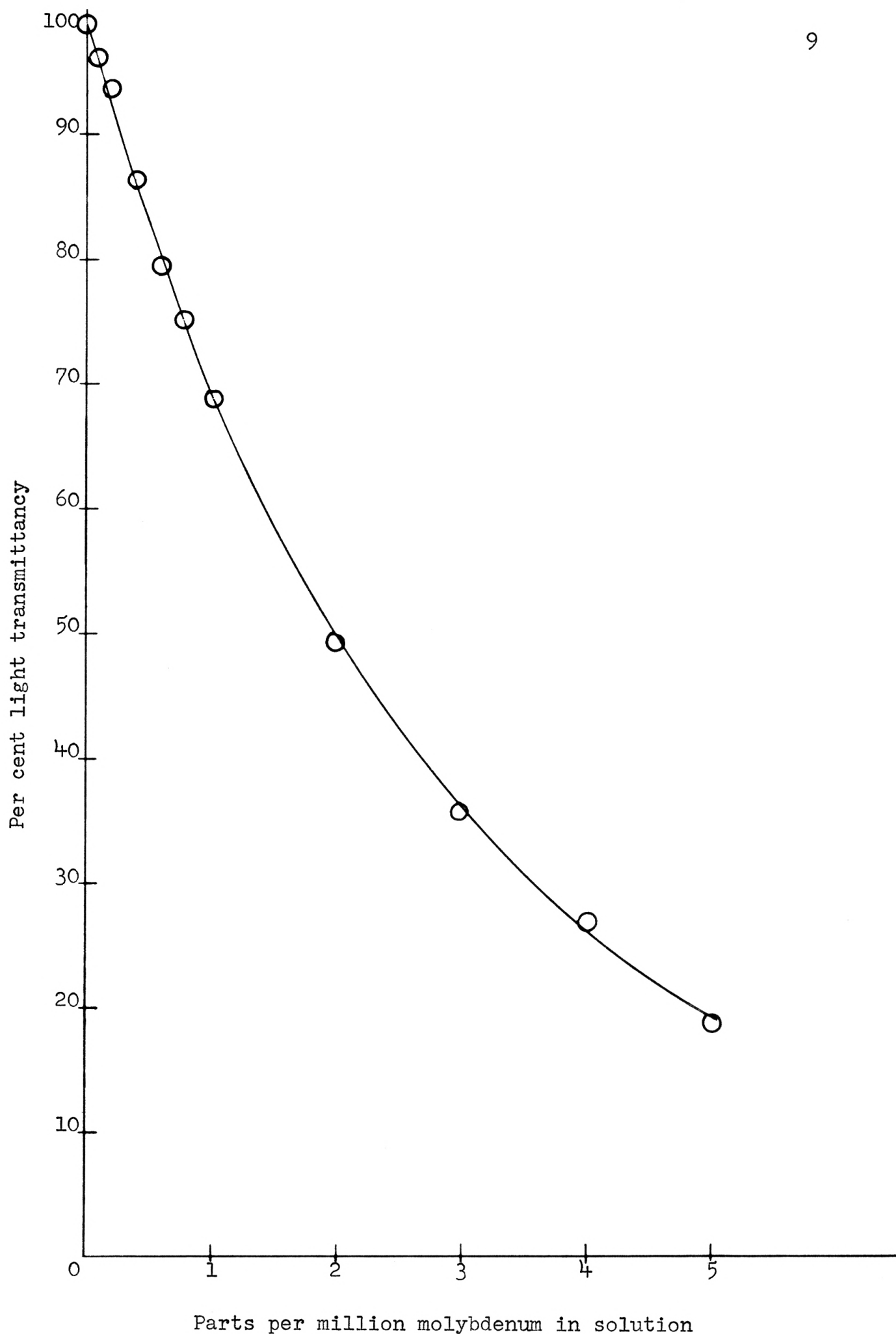


Fig. 1. Standard curve for use with an Evelyn photometer in determining parts per million molybdenum in solution. Air rest point of instrument used was 69.0 with a 420 millimicron filter.

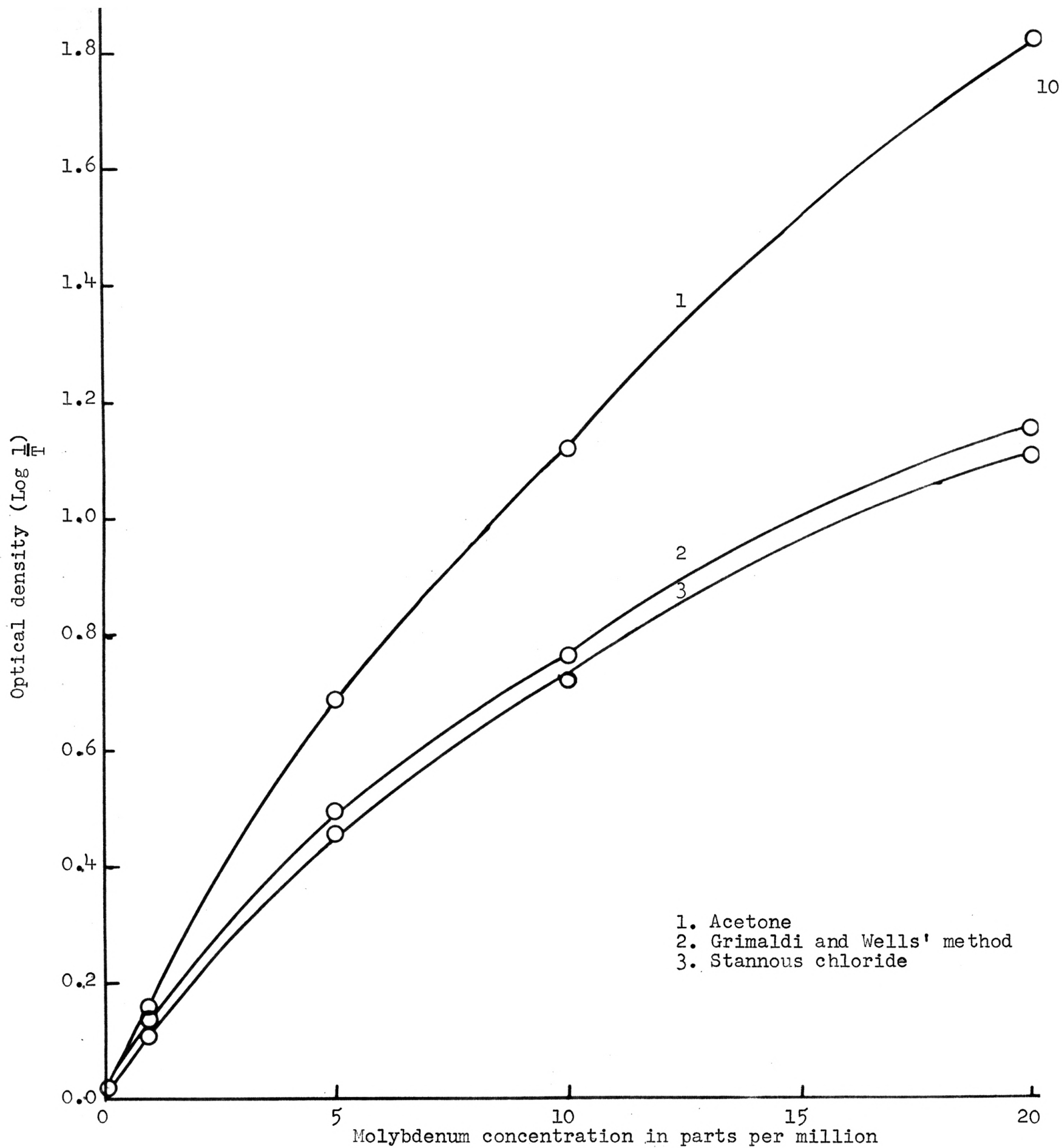


Fig. 2. Intensity of molybdenum color complex developed by different reducing agents.

Table 1. Transmittancies obtained with different concentrations of molybdenum and various reducing agents.^{1/}

Reducing agent :	: Molybdenum concentration in parts per million			
	1	5	10	20
Acetone	69.5	20.5	7.0	1.0
Stannous chloride	78.0	35.0	19.0	8.0
Camphor	99.0	73.0	71.0	58.0
NaHSO ₃	88.0	---	---	76.0
NaHSO ₃ & metol	76.8	71.0	68.3	56.0
1 amino-2-naphthol-4-sulfonic acid plus Na ₂ SO ₃ and Na ₂ S ₂ O ₅	72.5	71.0	68.5	67.3
Hydroxylamine hydrochloride	97.0	97.0	92.0	88.0

^{1/}Light transmittancies expressed in per cent.

an optical density of 0.20 using stannous chloride, 0.23 using the Grimaldi-Wells modification of the stannous chloride method, and 0.32 using acetone. The increase in color intensity was even greater at the higher concentrations of molybdenum.

Table 2 compares the influence of different reduction methods on the stability of the color complex. Color stability was obtained for a period of 48 hours at all concentrations of molybdenum tested when acetone was used as the reducing agent. Rapid fading of the color complex occurred with the other two reduction methods. A graphical comparison of the rate of fading of the color complex is shown in Fig. 3, where changes in transmittancy are plotted against time in minutes. All comparisons shown on the graph are for 5 ppm molybdenum. While a significant amount of fading occurred in 5 minutes and the color intensity was greatly diminished in one hour when stannous chloride was used as the reducing agent, acetone reduction produced an unchanging color.

Table 2. Comparison of per cent light transmittancies obtained with different reduction methods and various molybdenum concentrations at different time intervals after the development of the color complex.

Time	Molybdenum concentration in parts per million					
	0.0	0.1	1.0	5.0	10.0	20.0
Acetone reduction method						
1 minute	100.00	95.75	69.50	20.50	7.50	1.50
15 minutes	100.00	96.00	69.75	20.75	7.50	1.75
30 minutes	100.00	95.75	69.50	20.50	7.25	1.50
1 hour	100.00	96.00	69.75	20.50	7.25	1.50
16 hours	100.00	96.25	69.50	20.25	6.75	1.50
48 hours	100.00	95.50	69.50	20.00	6.50	1.50
Stannous chloride reduction method						
1 minute	100.00	97.25	78.00	35.00	19.00	8.00
15 minutes	100.00	97.25	81.50	44.00	28.00	15.00
30 minutes	100.00	97.50	83.25	48.50	32.00	17.00
1 hour	100.00	97.50	85.00	51.50	33.75	17.50
16 hours	100.00	99.00	97.75	82.25	67.25	43.50
48 hours	100.00	100.00	99.25	95.75	92.00	87.00
Grimaldi and Wells modification of stannous chloride method						
1 minute	100.00	95.50	73.00	32.00	17.50	7.00
15 minutes	100.00	96.00	74.00	36.00	23.00	12.00
30 minutes	100.00	96.50	75.00	40.00	27.00	17.00
1 hour	100.00	96.75	76.00	42.50	30.50	20.00
16 hours	100.00	96.25	84.50	63.75	52.50	40.50

Table 2 shows that the fading of the color complex after stannous chloride reduction was more rapid at higher concentrations; however, rapid fading was still encountered at concentrations of 1 ppm molybdenum.

Table 3. Effect of acidity on the development of the molybdenum color complex.^{1/}

Normality of final solution in: respect to hydrochloric acid : Per cent light transmittancy	
0.25	50.75
0.70	24.25
1.20	21.00
1.70	20.25
2.20	19.00

^{1/}Five parts per million molybdenum used for all determinations.

Table 3 brings out the fact that as in previous methods the acidity of the solution in which the molybdenum determination is carried out must be carefully controlled when acetone is used as the reducing agent. The results in Table 3 would seem to indicate that a Normality between 1.2 and 2.0 in respect to hydrochloric acid should be maintained in order to obtain accurate results. This is essentially the same as determined by Hurd and Allen (9) using stannous chloride. Table 3 also shows that a uniform acidity should be maintained in all standards and unknown solutions to eliminate small differences in color development.

Table 4. Effect of different acids on the development of the molybdenum color complex with solutions containing 5 ppm molybdenum.

Acid used ^{1/}	:	Per cent light transmittancy
Hydrochloric	:	19.00
Sulfuric	:	20.00
Nitric	:	59.75

^{1/}Final solutions 1.5 N in respect to all acids.

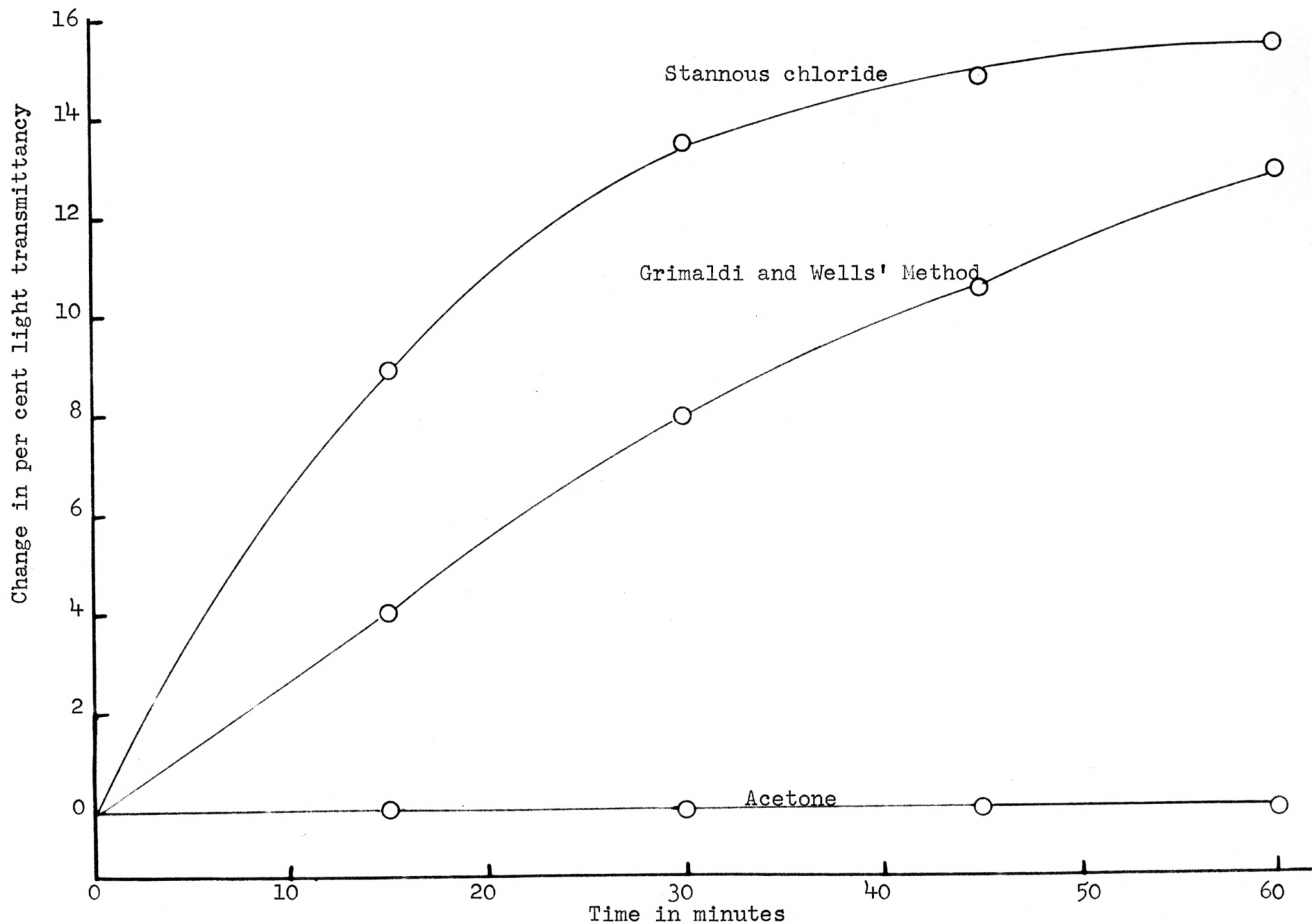


Fig. 3. Rate of fading of molybdenum color complex with different reduction methods. $\overline{41}$
Solutions contain 5 ppm molybdenum.

Table 4 shows that hydrochloric and sulfuric acids have essentially the same effect on the development of the color complex. Full color development was not obtained when nitric acid was used. Table 4 seems to indicate that any non-oxidizing acid should be satisfactory for the development of the color complex if the correct normality of the final solution in respect to acid is maintained.

Iron was the only interfering element investigated during the experimental work on determining molybdenum in solutions. However, it is assumed that elements interfering with the determination of molybdenum as the thiocyanate by other reducing methods will also interfere with the acetone reduction. Grimaldi and Wells (5) have devised a method for eliminating the interference of tungsten and vanadium. They have also found that phosphates interfere with the color reaction when tungsten is present in appreciable amounts and that large amounts of nitrates cause excessive fading. The fact that nitrates cause fading has been challenged by Barshad (2) who uses controlled amounts of nitrate ion to develop greater color intensity and reduce fading.

Table 5. Effect of time of heating at 70° C. on development of the color complex in solutions containing 5 parts per million molybdenum.

Time of heating in minutes	:	Light transmittancy in per cent
10		20.50
20		20.50
30		20.75
40		20.75
50		20.50
60		20.75

Table 5 compares transmittancy values obtained after various periods of heating during the reduction process. An examination of the table seems to indicate that heating for 10 minutes is sufficient for color development. It is recommended that heating be continued for 20 minutes to ensure full color development. This allows for the reduction of small amounts of ferric iron, and also allows for a range of temperatures from 60 to 70 degrees C. during the period of heating.

Table 6. Effect of solution temperatures on light transmittancy of the molybdenum color complex.^{1/}

Temperature in degrees C.	:	Light transmittancy in per cent
15	:	20.5
30	:	20.5
40	:	20.5

^{1/}Five parts per million molybdenum used for all comparisons.

Table 6 indicates that the temperature of the solutions at the time of reading may vary from 15 to 40 degrees C. without affecting the transmittancy values. Considerable variations in room temperature are, therefore, allowable.

DETERMINATION OF MOLYBDENUM IN SOILS

Experimental Methods

All molybdenum determinations were carried out by the acetone reduction method described in the previous section on determination of molybdenum in solutions. Different methods of extracting

molybdenum from soils were tested. Both the hydrofluoric acid volatilization method and the sodium carbonate fusion method were used in the experiment in an attempt to arrive at the total molybdenum content of soils. Ten per cent sodium hydroxide was used to extract alkali soluble molybdenum. Water, and 1 N ammonium acetate were used to extract molybdenum for the purpose of determining water soluble and available or exchangeable molybdenum.

Determination of Total Molybdenum

The hydrofluoric acid volatilization method outlined by Nichols and Rogers (12) and the sodium carbonate fusion method used by Robinson (14) were used as extraction methods for determining the total molybdenum content of soils. Table 7 shows the results of the analysis for total molybdenum. Both extraction methods were tried on the Geary silt loam soil. Table 7 shows that very poor agreement was obtained between the two methods. The determination of total molybdenum was very unsatisfactory in general. Agreement between replications and duplicate samples were very poor. The total molybdenum content of the two soils appear to be abnormally high when compared with total molybdenum contents of soils reported by other investigators. This fact would lead one to suspect that interference by other elements in the soil was being encountered. Known amounts of molybdenum were added to samples analyzed by the hydrofluoric acid volatilization method. The percentage of

recovery was very erratic, and 75 per cent was the maximum obtained. Since molybdenum hexafluoride volatilizes at 18° C. this might account for some of the error. The accuracy of the method might be increased to a great extent if the volatilization process were carried out at lower temperatures for extended period of time. The fact that a Meker burner was used as a source of heat might explain some of the erratic results obtained, since variations in temperature apparently affect the volatilization process. About the only conclusion that can be drawn from the results on total molybdenum determinations is the fact that more experimental work needs to be done before the data can be of much value.

Table 7. Total molybdenum content of Kansas soils determined by two extraction methods.

Soil type	Parts per million molybdenum in soil	
	Hydrofluoric acid	Sodium carbonate
	volatilization	fusion
Geary silt loam	45.0	36.0
Colby silt loam	----	18.0

Determination of Alkali Soluble Molybdenum

Ten grams of air dry soil were used for the determination of alkali soluble molybdenum. The soil was ignited at 600 to 700 degrees C. for 30 minutes to destroy the organic matter. The ignited soil was then extracted with 20 ml of 10 per cent sodium hydroxide. After heating to boiling, the solution was filtered, neutralized with hydrochloric acid, and evaporated to

dryness. The residue was then taken up with hydrochloric acid and filtered again to remove silica. Molybdenum was then determined by the acetone reduction method.

Table 8. Alkali soluble molybdenum content of Kansas soils.

Soil type	County	Molybdenum content of soil in parts per million
Geary silt loam	Riley	1.60
Cherokee silt loam	Cherokee	1.50
Sherman silt loam	Thomas	1.20
Munjor silty clay loam	Ellis	1.00
Not classified	Greeley	1.10
Not classified	Kearny	1.60
Colby silt loam	Finney	1.40

Table 8 shows that the two Eastern Kansas soils, represented by the Geary silt loam and the Cherokee silt loam, have approximately the same alkali soluble molybdenum content. This is probably not significant since only two soils were tested. Western Kansas soils show considerable variation. A greater number of soils would have to be sampled before any conclusions could be reached as to whether molybdenum content is associated with soil type. Table 8 also shows that none of the soils tested have high alkali soluble molybdenum contents.

Determination of Water Soluble and Ammonium Acetate Extractable Molybdenum

Ten grams of air dry soil were used for both determinations. Organic matter was either destroyed by igniting the soil or by treating the extracted solutions with nitric and hydrochloric acids. The two methods of removing organic matter gave comparable

results. Water soluble molybdenum was determined by adding 100 ml of distilled water to the soil, and available or exchangeable molybdenum was determined by adding 100 ml of 1 N ammonium acetate adjusted to pH 7. All samples were shaken for 30 minutes on an end over end shaker, filtered, evaporated to dryness, and taken up with hydrochloric acid. The molybdenum was then determined by the acetone reduction method.

Table 9. Water soluble and ammonium acetate extractable molybdenum content of Kansas soils.

Soil type	:	County	Molybdenum content in ppm	
			Water soluble	:Ammonium acetate extractable
Geary silt loam		Riley	0.75	1.45
Colby silt loam		Finney	0.50	1.25
Not classified		Greeley	0.40	0.80

The data presented in Table 9 show that the amount of molybdenum extracted with ammonium acetate was in all cases significantly greater than the amount of water soluble molybdenum determined in the same soil. Since 1 N ammonium acetate is used by many investigators for the determination of exchangeable bases, this would suggest that part of the molybdenum in the soil is held as an exchangeable cation on the colloidal complex. The fact that molybdenum may exist as an exchangeable ion is important since investigators have not considered molybdenum when exchangeable bases are determined in soils. Table 9 also shows that the water soluble molybdenum content of Kansas soils is not very high. Using the data obtained by Barshad (3) as a criterion it is highly

improbable that there would be any danger of forage grown on the Kansas soils tested producing the molybdenum disease of livestock.

Table 10 shows that organic matter interferes with the determination of molybdenum in soils. Since organic matter caused some degree of interference with all extraction methods tested, it is essential that it be destroyed if accurate results are to be obtained.

Table 10. Effect of organic matter on the determination of ammonium acetate extractable molybdenum.

Soil type	:Parts per million of molybdenum found in soil		
	:Untreated samples	: Soil ignited	: Extr. sol. treated with :HNO ₃ & HCl
Geary silt loam	9.0	1.45	1.50
Colby silt loam	6.0	1.25	1.28

SUMMARY

The experiment was designed for the purpose of making a preliminary survey of the molybdenum content of Kansas soils. It was felt that a study of the molybdenum content of Kansas soils would be of value since the evidence is mounting that either a deficiency or an excess of molybdenum in soils may present problems. There are indications that molybdenum may be an essential or at least a beneficial element for plant growth. Excess quantities of molybdenum are known to be toxic to plants and animals. Since either a deficiency or an excess of molybdenum may present problems, it seemed highly desirable to determine if

either situation existed in Kansas soils.

Shortly after the experimental work was started it became apparent that existing colorimetric methods of molybdenum determination should be modified in order to adapt their use to photoelectric instruments. The main difficulty encountered with existing methods was the fact that rapid fading of the color complex occurred when stannous chloride was used as the reducing agent. Therefore, a method was developed in which acetone is used as the reducing agent and by which color stability is obtained for a period of 48 hours. The sensitivity of the determination is also increased over previous methods.

The following conclusions can be drawn from the molybdenum determinations in Kansas soils:

1. The results of the determination of total molybdenum are very unsatisfactory. More experimental work needs to be done on the determination before the information obtained can be of any value.

2. Alkali soluble molybdenum contents of Kansas soils indicate that the amount of alkali soluble molybdenum is not excessive.

3. The fact that the amounts of molybdenum extracted by 1 N ammonium acetate are significantly greater than the amounts of molybdenum extracted by water from the same soils suggests that molybdenum may be held as a replaceable ion on the colloidal complex.

4. The amount of water soluble molybdenum found in the Kansas soils tested would indicate that sufficient molybdenum

is present for plant growth if molybdenum is a beneficial element.

5. Using the data obtained by Barshad (3) as a criterion, it is highly improbable that forage grown on the soils tested would cause the molybdenum disease of livestock. The water soluble molybdenum content of the soils tested is lower than the values Barshad found for soils in the areas where the molybdenum disease is common.

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REFERENCES

- (1) Arnon, D. I., and P. R. Stout.
Molybdenum as an essential element for higher plants.
Plant Physiol. 14: 599-602. 1934.
- (2) Barshad, I.
Molybdenum determination in plant material; modification
of thiocyanate stannous chloride method. Anal. Chem.
21: 1148-1150. 1949.
- (3) Barshad, I.
Molybdenum content of pasture plants in relation to
toxicity to cattle. Soil Sci. 66: 187-195. 1948.
- (4) Ferguson, W. S., A. H. Lewis and S. J. Watson.
The teart pastures of Somerset. Jour. Agr. Sci. 33: 44-51.
1943.
- (5) Grimaldi, F. S., and R. C. Wells.
Determination of small amounts of molybdenum in tungsten
and molybdenum ores. Indus. Engg. Chem. Analyt. Ed. 15:
315-316. 1943.
- (6) Hiskey, C. F., and V. W. Meloche.
The nature of the thiocyanate complex of molybdenum.
Amer. Chem. Soc. Jour. 62: 1565-1574. 1940.
- (7) Hiskey, C. F., and V. W. Meloche.
Color phenomena associated with quinquevalent molybdenum
solutions. 11. The effects of various electrolytes.
Amer. Chem. Soc. Jour. 63: 964-969. 1941.
- (8) Horner, C. K., et. al.
Nitrogen fixation by azotobacter as influenced by
molybdenum and vanadium. Jour. Agr. Res. 65: 173-193.
1942.
- (9) Hurd, L. C., and H. O. Allen.
Colorimetric determination of molybdenum; a study of
variables involved. Indus. Engg. Chem. Analyt. Ed. 7:
396-398. 1935.
- (10) Jensen, H. L., and R. C. Betty.
Nitrogen fixation in leguminous plants. 111. The
importance of molybdenum in symbiotic nitrogen fixation.
Linn. Soc. N. S. Wales Proc. 68: 1-8. 1943.
- (11) Mulder, E. G.
Importance of molybdenum in the nitrogen metabolism of
microorganisms and higher plants. Plant and Soil.
1: 94-119. 1948.

- (12) Nichols, M. L., and L. H. Rogers.
Determination of small amounts of molybdenum in plants and soils. Indus. Engg. Chem. Analyt. Ed. 16: 137-140. 1944.
- (13) Perrin, D. D.
Determination of molybdenum in soils. New Zealand Jour. Sci. and Technol. 28A: 183-187. 1946.
- (14) Robinson, W. O.
Determination of vanadium and molybdenum in soils. Soil Sci. 59: 91-92. 1945.
- (15) Sandell, E. B.
Determination of chromium, vanadium, and molybdenum in silicate rocks. Indus. Engg. Chem. Analyt. Ed. 8: 336-341. 1936.
- (16) Sandell, E. B.
Colorimetric determination of traces of metals. New York. Interscience Publishers. 1944.
- (17) Scott, W. W.
Standard methods of chemical analysis. New York. D. Van. Nostrand Co. 1944.
- (18) Stanfield, K. E.
Determination of molybdenum in plants and soils. Indus. Engg. Chem. Analyt. Ed. 7: 273-274. 1935.