DEPARTMENT OF COMMERCE

Bureau of Standards

Certificate of Analyses

OF

STANDARD SAMPLE No. 71

CALCIUM MOLYBDATE

[All results are based on a sample dried for one hour at 125° C.]

ANALYST*	Molybdenum	Iron	Titanium
1	35. 29[a] 35. 27[b] 35. 23[c]	1. 92	0. 06
2	35. 29[b]	1. 92	. 07
3	35. 35[a] 35. 38[b]	1. 92	. 06
4	35. 40[a]		
5	35. 22[a]		
6	35. 40[a]		
7	35. 19[a] 35. 24[c]		
8	35. 30[a] 35. 24[b]		
9	35. 28[b] 35. 32[d]		
Averages	35. 29[e]	1. 92	. 063
Recommended Values	35. 3	1. 92	. 06[f]

[a] Iron and titanium separated by double precipitation with ammonium hydroxide, the solution acidified, and subsequently reduced in a Jones reductor and titrated with 0.1 *N* $KMnO_4$.

[b] Complete sulphuric acid solution of the sample reduced in a Jones reductor and the result corrected for iron and titanium. No other metals reducible in the Jones reductor were detected.

[c] Gravimetric, precipitated as MoS_3 weighed as MoO_3.

[d] Precipitated as MoS_3 and subsequently dissolved and reduced in Jones reductor.

[e] The atomic weight 96.0 was used for Molybdenum in all calculations.

[f] Values for constituents not established as accurately as the above values are: $CaO = 22.0$ per cent, $SiO_2 = 17.5$ per cent, $SO_3 = 0.40$ per cent. $Na_2O = 1.5$ per cent and $K_2O = 0.45$ per cent.

*LIST OF ANALYSTS

1. H. A. Bright, Bureau of Standards.
2. James I. Hoffman, Bureau of Standards.
3. W. C. Fedde, Bureau of Standards.
4. Oscar Smith, The York Metal & Alloys Co., York, Pa.
5. W. D. Brown, The Carnegie Steel Co., Duquesne, Pa.
6. C. E. Nesbitt, The Carnegie Steel Co., Braddock, Pa.
7. Molybdenum Corporation of America, E. A. Lucas, works manager, Washington, Pa.
8. H. N. Fry and C. Harwood, Electro Metallurgical Co., Niagara Falls, N. Y.
9. R. J. Price and T. R. Cunningham, Electro Metallurgical Co., New York, N. Y.

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George K. Burgess
Director.

(See other side)

SUGGESTED METHOD FOR THE DETERMINATION OF MOLYBDENUM IN CALCIUM MOLYBDATE

In this method the iron, titanium, arsenic, and vanadium, are separated from molybdenum by double precipitation with ammonium hydroxide. The combined filtrates are then acidified, the molybdenum reduced by zinc in a Jones reductor and reoxidized by titration with a standard solution of potassium permanganate.

SOLUTIONS REQUIRED

Standard Potassium Permanganate.—Dissolve 3.2 g of potassium permanganate in 1,000 ml of distilled water, allow to age for at least 10 days and filter through purified asbestos. Standardize the permanganate solution against Bureau of Standards standard sodium oxalate as follows:

In a 400 ml beaker dissolve 0.28 to 0.30 g of sodium oxalate in 200 ml of hot water (80 to 90° C.) and add 10 ml of dilute sulphuric acid (1:1). Titrate at once with the permanganate solution, stirring the liquid vigorously and continuously. The permanganate must not be added more rapidly than 10 to 15 ml per minute, and the last 0.5 to 1 ml must be added dropwise, with particular care to allow each drop to be fully decolorized before the next is introduced. The excess of permanganate used to cause an end point color must be estimated by matching the color in another beaker containing the same bulk of acid and hot water. The temperature of the solution should not be below 60° C. by the time the end point is reached. One milliliter of 0.1 N $KMnO_4 = 0.0032$ g of molybdenum.

Ferric sulphate.—Dissolve 100 g of $Fe_2(SO_4)_3$ in 500 ml of water containing 175 ml of phosphoric acid (sp. gr. 1.70). Dilute to 1 liter.

PROCEDURE.—As the dried sample is hydroscopic, samples for the determination of molybdenum should be taken by either of the following procedures:

(*a*) Transfer the approximate amount of sample, 0.5 to 0.6 g to a small glass weighing bottle provided with a ground glass stopper. Heat the bottle and contents, together with a similar bottle with stopper, at a temperature of 125° C. for one hour. Stopper the bottles and cool in a desiccator containing a good desiccant. Weigh the bottle and contents against the empty bottle as a tare, loosening the stoppers for an instant to equalize the pressure before weighing. Carefully transfer the sample from the weighing bottle to a 400 ml beaker and again weigh the bottle, which usually contains a small film of untransferred sample. The difference in weight represents the exact weight of dried sample taken for analysis.

(*b*) Weigh a portion of the well-mixed, air-dried sample and make a special moisture determination on a 2 g sample taken at the same time and dried at 125° C. for one hour. The molybdenum value obtained for the air-dry sample must then be corrected as indicated by the loss in weight of the sample dried at 125° C.

Where sufficient sample is available method (*b*) is preferable.

Decompose the sample by heating with 25 ml of dilute hydrochloric acid (2:1). Cool, add 20 ml of dilute sulphuric acid (1:1) and carefully evaporate to fumes of sulphuric acid. Cool, dilute with 60 ml of water and heat gently for 10 to 15 minutes. Filter off the insoluble matter which is chiefly silica and wash well with hot water. Acid attack of the Bureau's Standard Calcium Molybdate No. 71 leaves a small amount of molybdenum, about 0.04 to 0.07 per cent, in the insoluble matter. To recover this molybdenum ignite the insoluble residue in a platinum crucible at a temperature not over 500° C., above which molybdenum will be volatilized. Treat the ignited residue with sulphuric and hydrofluoric acids to expel silica, and fuse the nonvolatile residue with 3 g of sodium carbonate. Dissolve the melt in 50 ml of dilute sulphuric acid (1:9) and add the solution to the main solution.

Adjust the volume of the combined solutions to 150 ml and add enough of a solution of ferric sulphate to have a tenfold excess of iron over the amount of arsenic present—0.08 to 0.1 g of iron is sufficient for most calcium molybdates.

Add ammonium hydroxide until most of the acid has been neutralized, but avoid adding so much that the color of the solution changes to an amber tint. Heat the solution to 90° C. and pour it very slowly, while stirring vigorously, into 85 ml of warm dilute ammonium hydroxide (15 ml of ammonium hydroxide, sp. gr. 0.90 and 70 ml of water.) Let the precipitate settle, filter and wash the residue with hot water. Reserve the filtrate. Dissolve the precipitate in a slight excess of hot dilute sulphuric acid, nearly neutralize with ammonium hydroxide and pour the solution into 85 ml of warm dilute ammonium hydroxide as before. Allow the precipitate to settle, filter, and wash the residue.

Combine the two filtrates, which should now contain all of the molybdenum (see note 1) and evaporate to 200 ml. Add sulphuric acid until the solution contains 5 ml of acid per 100 ml, add enough of a saturated solution of potassium permanganate to give a permanent pink color, and heat to boiling. Cool the solution to 40° C. and slowly pass it through a Jones reductor and into a receiving flask containing five times more ferric iron, as ferric sulphate, than is theoretically required to oxidize the molybdenum from the trivalent to the sexivalent state. Thirty-five ml of the ferric sulphate will usually suffice. Wash the reductor with 100 ml of dilute sulphuric acid (5:95) and 100 ml of water. Titrate with 0.1 N potassium permanganate. Subtract the volume of permanganate required by a determination on the reagents which have been carried through the whole procedure. The molybdenum is reduced from Mo^{VI} to Mo^{III} and then reoxidized by the permanganate to Mo^{VI}.

NOTES

1. Standard sample No. 71 contains only traces of tungsten and vanadium. With calcium molybdates that contain significant quantities of these elements the combined ammoniacal filtrates must be treated as follows before reduction in the Jones reductor: Add 1 g of tartaric acid, warm and saturate the solution with hydrogen sulphide. Make slightly acid (2 per cent) with sulphuric acid, stir well, digest for one hour at 70° C. and filter. Wash with dilute sulphuric acid (1:99) which has been saturated with hydrogen sulphide. For umpire work, boil the filtrate to remove hydrogen sulphide, oxidize any remaining molybdenum with ammonium persulphate and treat the solution with hydrogen sulphide. If any molybdenum sulphide is obtained the solution should be filtered and the precipitate added to the first precipitate. Treat the precipitate and paper with 10 ml of sulphuric acid (sp. gr. 1.84) and 10 ml of nitric acid (sp. gr. 142) in a 600 ml beaker and cautiously evaporate to fumes of sulphuric acid. Cool, add 10 ml of nitric acid (sp. gr. 1.42) and again evaporate to fumes of sulphuric acid. Cool and repeat the evaporation with nitric acid until every trace of yellow color due to carbonaceous matter has disappeared. When this has been accomplished, fume strongly for a few minutes, cool, wash down the sides of the beaker and again fume strongly in order to completely remove nitric acid. Cover the beaker and to the warm solution very cautiously add dropwise a saturated solution of potassium permanganate until in excess. Cool, dilute to 175 ml, warm to 40° C., and reduce in the Jones reductor.

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