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SEPARATION AND RADIOCHEMICAL STUDY OF MOLYBDIC AND TUNGSTIC OXIDES

by

John Hotchkiss Boles III U.C. 1964

Senior Thesis Submitted
in Partial Fulfillment
of the Requirements of Graduation

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UNION COLLEGE
MAY 1964

This Thesis

Submitted by

John Hotchkiss Boles

John Hotchkiss Boles

to the

Department of Chemistry of Union College

in partial fulfillment of the requirements of the degree of

Bachelor of Science with a Major in Chemistry

is approved by

C F Weick

(Signature of Research Adviser)

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INTRODUCTION
and
BACKGROUND

A common difficulty in the industrial purification of metals is that of separating molybdenum from tungsten. It seems that no matter what procedure is used, these two elements always co-precipitate.

With the closing of China to the free world by the Communists, effectively 90 per cent of the good grade of tungsten ore (wolframite) in the world is closed and unattainable. This act leaves only poor grade scheelite really open to the United States for mining. Scheelite usually has ores of molybdenum in it. For most purposes the two substances may be effectively separated through commercial means, but for tungsten filaments there must be no more than .001 per cent molybdenum in the tungsten.

During the last decade the General Electric Corporation has had to rely more and more often on the poorer grades of tungsten found in the western hemisphere for their electrical apparatus. General Electric has made great advances in getting pure filament tungsten though the method is not known by the general public. However, the company did little in reporting quantitative data about the analysis. Also, there has been no reliable work done on determining, if any, the crystal structure of the complexed oxides or the type of co-precipitation involved.

Generally, molybdenum and tungsten are separated and analyzed as the trioxide; i.e. in their +6 oxidation state. It would seem to be only a matter of heating the precipitated oxides of tungsten and molybdenum to effect a separation of the two since MoO_3 sublimes at $700^{\circ}C$ (1), 100° below that of WO_3 ($800^{\circ}C$)(2); however, a good separation cannot be obtained (3).

One possible explanation of this phenomenon which has been offered is suggested indirectly by M. G. Ingraham (4) in 1959. Using mass spectrophotometry he found that pure MoO_3 could become Mo_3O_9 at $750^{\circ}C$. The complexing of the oxides of molybdenum is common at higher temperatures (5) and may be a clue to the answer of the problem. Ingraham suggested it be possible that tungsten atoms might replace some of the molybdenum atoms in the crystal lattice upon complexing at high temperatures.

Analysis of the tungsten content of the vaporized molybdenum trioxide was first attempted using wet chemical procedures (5). This method proved ineffectual. A method proposed a year later by Samuel Wales, a General Electric research student on a summer grant, is neutron irradiation analysis (6).

According to his paper he effectively separated the two oxides in an oven from a mechanical mixture. The volatilized oxide was collected, irradiated with thermal neutrons and the tungsten concentration measured.

Wales also noted that upon condensation of the volatilized oxides bands of oxides were formed along the condensing tube of the oven. He did not suggest why this phenomenon was so, but it probably occurred because of the formation of different oxides of molybdenum upon heating above 700° C (6).

In the work presented here, tungsten and molybdenum are precipitated and chemically separated as much as is possible. The products are collected and irradiated with thermal neutrons and the concentration of tungsten determined. In this way only that tungsten forming a complex or dissolving into the molybdenum crystal will be measured.

This study suggested by the chemists at the General Electric Research Laboratories, will be made into possible structures of complex oxides of molybdenum and tungsten to try to explain their inseparableness. Also, the type of co-precipitation in relation to conditions under which the molybdenum and tungsten are precipitated will be suggested. Whenever possible, quantitative data will be presented by graphs or tables in relation to the precipitation and neutron activation of molybdenum and tungsten.

CHAPTER I

THEORY

Since a good organic precipitation of molybdenum can be made with α benzoin oxime (1)(2)(3), this route is taken for the preparation of the samples for irradiation. The following general procedure is now proposed to co-precipitate the molybdenum and tungsten.

Samples of dry molybdic oxide are weighed out and a very small amount of tungstic oxide is added. The oxides are dissolved in ammonium hydroxide or dilute sodium hydroxide. The two substances readily form molydates or tungstates. The solution is acidified with hydrochloric acid and any tungstic acid that precipitates is filtered off. Cinchonine solution is added to insure complete precipitation of tungsten. This separation of tungsten serves to remove as much as is chemically possible and any remaining in solution will be brought down with the molybdenum in the crystal lattice when the molybdenum is precipitated. Sulphuric acid is added since α benzoin oxime precipitates molybdenum best in a sulphuric acid media. An alcoholic solution of α benzoin oxime is added along with bromine water to precipitate the molybdenum. The solution is kept cold (5-10° C.) and colored with bromine to keep the metal ion in its highest oxidation state (VI). After filtering the gelatinous precipitate it is heated in an oxidizing atmosphere in a muffle furnace to molybdic oxide. The sample is now ready for irradiation.

Alternately a study can be made on molybdenum coprecipitating with tungsten and after proper separation of as much molybdenum as possible the sample is irradiated.

A radioactive nuclide of relatively short half life can generally be detected with low background down to a weight of a few micrograms. With this supposition the concentration of tungstic oxide in molybdic oxide can be detected after precipitation of the metals. In previous work by Wales (6), and Dams and Hoste (7) this fact is borne out. Wales (6) shows that tungsten in molybdenum can be detected in a mechanical mixture which has been volatilized at 700° C. then irradiated with slow neutrons. Dams and Hoste's (7) work deals in recovery of and detection of molybdenum and tungsten through acidic and organic precipitates of radioactive tracers.

The half life and cross-section data are in support of this method. The possible products of thermal neutron activation taking into consideration isotope abundance, cross-section and half life is summarized in the table below:

TABLE I

Target	Abundance	X-section	$t_{\frac{1}{2}}$	Active Isotope
Mo^{98}	24.60	0.13 ± .05 barns	67 hr	Mo^{99}
Mo^{100}	9.68	0.20 ± .05	14.6 min	Mo^{101}
W^{180}	0.126	10 ± 10	140 d	W^{181}
W^{184}	30.64	2.1 ± 0.6	73 d	W^{185}
W^{186}	28.64	34 ± 7	24.1 hr	W^{187}

Handbook of Chem. and Phys., 40th ed., 1958-1959.

W^{186} is the logical target nuclide because of its much greater cross-section and the relatively short half life of W^{187}. Little activity should be obtained from the other nuclides due to either low cross-sections, long half life, or low abundance.

Knowing the neutron flux and time of irradiation and making proper corrections for counting yield the amount of tungsten that co-precipitated with the molybdenum can be calculated after measurement of the count rate.

In the alternate method of determining the amount of molybdenum co-precipitating with tungsten it is proposed that 14 MeV neutrons be used for irradiation. Tungsten has a low cross-section for 14 Mev neutrons, while that of molybdenum is relatively high.

TABLE II

Target	X-section	$t_{\frac{1}{2}}$	Active Isotope
Mo^{92}	0.19 barns	15.5 min	Mo^{91}
Mo^{97}	0.11 ± 0.05	72 min	Nb^{97}
W^{186}	none	--	--

Picker Scintillator, Vol. VI, No. 5, June 15, 1963.

By the same procedure mentioned above the amount of molybdenum co-precipitating can be calculated.

From subsequent measurements of weight or percentage of co-precipitant and type of precipitation; i.e. fast or slow, postulations as to the type of mechanism by which the tungsten enters the molybdic oxide crystal and visa versa and to the nature of the structure of the crystal can be made (8).

CHAPTER II

EXPERIMENTAL DATA and RESULTS

CHEMICAL PREPARATION

The procedure followed in the chemical preparation of molybdenum and tungsten is commercially standard but is changed somewhat to suit the needs of this work (1)(2)(3).

The first step involved finding the percentage recovery of molybdenum using the α benzoin oxime precipitation method. Three test samples of approximately 0.05 grams were precipitated to test the procedure roughly outlined in Chapter I. Poor recovery resulted in lowering of the sample weight and more careful precipitation. Nine precipitations were made with sample weights from 0.0250 grams to 0.0453 grams. The following recovery percentages are noted in Table III:

TABLE III

Sample Wt.	% Recovery	Sample Wt.	% Recovery
0.0500 gm	80	0.0453	108
0.0514	--	0.0295	100
0.0520	90	0.0304	99
0.0284	105	0.0304	107
0.0347	99	0.0250	104
0.0305	108	0.0297	105

The average is 104 ± 3 per cent. The high percentage is almost within the experimental error if one assumes just a mechanical error in the Mettler balance of ± 0.0002 grams. Due to such small amounts of oxide the deviation from an ideal of 100 per cent can be expected.* Since the error is great and reproducibility is difficult with such small amounts of molybdic oxide, it was decided to use larger amounts of molybdic oxide.

At this point tungstic oxide was introduced to the molybdic oxide to see if a good recovery could be obtained after separation of the tungsten. Much time was lost in finding a solvent to dissolve the two oxides mutually. A few milliliters of concentrated sodium hydroxide dissolves the two quickly. The tungsten is then precipitated with the addition of 6M sulphuric acid. Sulphuric is not as good as nitric acid in precipitating tungstic acid (7), but the molybdenum precipitates better with α benzoin oxime in the presence of sulphuric acid. Further removal of tungsten is effected by the addition of drops of 12.5 per cent solution of cinchonine, which will not precipitate molybdenum, until no more yellow precipitate appears. This precipitate

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*Upon further work in precipitation it was found that some of the product was inorganic salt which came from a poorly washed ppt. This might account for the increase in product weight.

is filtered off with S & S No. 589 white ribbon paper. Then the filtrate is cooled to 5-10° C. and a 2 per cent α benzoin oxime solution in absolute alcohol is added to precipitate the molybdenum. Five milliliters of α benzoin oxime solution is added for the first 0.01 grams of molybdic oxide and three milliliters for each 0.01 grams thereafter. During the time of precipitation bromine water is added to impart a slight yellow color to the precipitate before adding to the filter. The precipitate is filtered on S & S No. 589 black ribbon paper and heated to the oxide in a muffle furnace at 550° C.* This temperature should be controlled carefully since molybdic oxide sublimes at 700°C. (6).

The results obtained from five samples ranging in weight from 0.2309 grams to 0.3157 grams with a slight amount of tungstic oxide added were poor. No tungsten would precipitate from sample 1 and very little from sample 2. Not enough sulphuric acid was added. Samples 3, 4 and 5 gave good precipitations of tungstic acid, but there was no recovery of molybdic oxide in sample 3. A white crystalline

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*During the course of initial experimentation S & S No. 589 black ribbon filter paper was found to be far superior to Whatman No. 41. Though they are comparable papers, the S & S leaves no ash whereas the Whatman leaves a considerable amount.

solid was left behind after heating which must come from insufficient washing of the sodium salts from the precipitate. Though this factor was corrected, the recovery of molybdic oxide was not decidedly improved. Some oxide was recovered from samples 4 and 5.

A light grey deposit on the inside of the crucibles of all the samples is the probable answer to the lack of oxide recovery. The molybdic oxide is being reduced probably by the filter paper. If this is the case, then an artificial oxidizing atmosphere will have to be created around the crucible. Oxygen flowing over the crucible mouth might solve the problem.

ACTIVATION ANALYSIS

In order to see what to expect in the way of neutron activation products samples of molybdic oxide and tungstic oxide were irradiated. The irradiation was carried out on a High Voltage Engineering Corporation Van de Graff accelerator. The accelerator uses water to slow the 14 Mev neutrons to thermal energies. Expected activities can be calculated from the equation:

$$A = N \phi \sigma (1 - \exp (-0.693 \, t/T_{\frac{1}{2}}) \qquad (1)$$

where A = disintegration rate
N = number of atoms in sample
= neutron flux (neutrons cm^{-2} sec^{-1})
= activation cross-section
t = time of irradiation
$t_{\frac{1}{2}}$ = half-life of the product nuclide

A fifteen minute irradiation of the 0.8860 gram tungsten sample produced a spectra showing only W^{187} (see Plate I and Graph I). The initial activity on the graph is due to a slight amount of molybdenum in the sample. The spectra were obtained on a RIDL Model 34-25 scintillation spectrometer and printed out on a Moseley Autograf X-Y recorder. The tungsten sample did not give a high enough activity with the sodium iodide well-type crystal using a fifteen minute irradiation and a neutron flux of 10^8 neutrons cm^{-2} sec^{-1} to be used for accurate tracer work. To be more useful one must have a higher flux or a much longer irradiation time.

The irradiation of molybdenum did not give as clear results. See Plates II and III. The 0.3 Mev peak can easily be identified as that of either Mo^{101} or Tc^{101} since both nuclides have this energy peak in abundance. A 0.478 Mev peak is due to the slight amount of tungsten contaminant. However, the 0.14 Mev peak cannot be explained. Tc^{99} has a peak of this energy but this nuclide would only be produced from a long irradiation time since the parent, Mo^{99}, has a long half life. This peak also drops more quickly in relation to the other peaks after an hour's decay. See Plate III. The half-life data supports the characteristic peaks of Plate II. See Graph II. Mo^{101} and Tc^{101} are in secular equilibrium being a special case where the half lives are equal. Graph II shows from the long-lived activity of 24 hours that some tungsten impurity is present in the sample. This graph also shows that the concentrations of the two substances can be determined simultaneously.

As is mentioned in the previous paragraph, one might expect some Mo^{99} to show up in the spectra; but due to its 66 hour half-life, the activity produced with a fifteen minute irradiation is negligible.

The important factor learned here is that due to the half-life of Mo^{101} a short irradiation gives a high activity even though one may have small amounts.

It is interesting to note the sensitivity of activation analysis under various conditions. Certain criteria are set forth first. Counting beta radiation rather than gamma proved to be more effective since one works with a background usually a factor of ten less with a Geiger counter than that of a scintillation counter. The background for the organic gas type of end window Geiger counter used in this work is thirty counts per minute. One therefore would need a count rate of about one hundred counts. Since the counting yield is about 10 per cent, a disintegration rate of 1000 disintegrations per minute is the minimum for reasonable precision. Table IV summarizes the sensitivity under various neutron fluxes and irradiation times.

Calculations are made from the following equation:

$$G = \frac{AW}{PN\phi\sigma\,(1 - \exp(-0.693\,t/T_{\frac{1}{2}}))} \qquad (2)$$

where

G = weight in grams of the oxide

P = % abundance of particular isotope

N = Avogadro's number

W = molecular weight of the oxide

all other symbols are the same as in Eq. 1.

TABLE IV

Sample	Irradiation Time	Neutron Flux	Minimum Sensitivity
MoO_3	15 min.	10^8 n $cm^{-2}sec^{-1}$	250 mg
MoO_3	1 hr. (saturation)	10^8	125 mg
MoO_3	15 min.	10^{12}	0.025 mg
MoO_3	1 hr. (sat.)	10^{12}	0.0125 mg
WO_3	15 min.	10^8	47.2 mg
WO_3	1 hr.	10^8	12.1 mg
WO_3	15 min.	10^{12}	4.72 μg
WO_3	1 hr.	10^{12}	1.21 μg
WO_3	24 hrs.	10^{12}	0.0675 μg

Under the proper conditions great sensitivity can theoretically be obtained.

CHAPTER III

CONCLUSION

Though a reliable method for the precipitation of molybdenum with traces of tungsten was not found, a start toward a method has been made. Work by Dams and Hoste (7) shed much light on the problem. Their work leads to further suggestions in the improvement of the method. Since molybdenum co-precipitates to a large extent with tungsten upon addition of acid, it is suggested that the molybdenum and tungsten first be precipitated at the same time, heated to the oxides, redissolved in ammonium hydroxide and the tungsten separated by the addition of acid or cinchonine and the molybdenum reprecipitated.

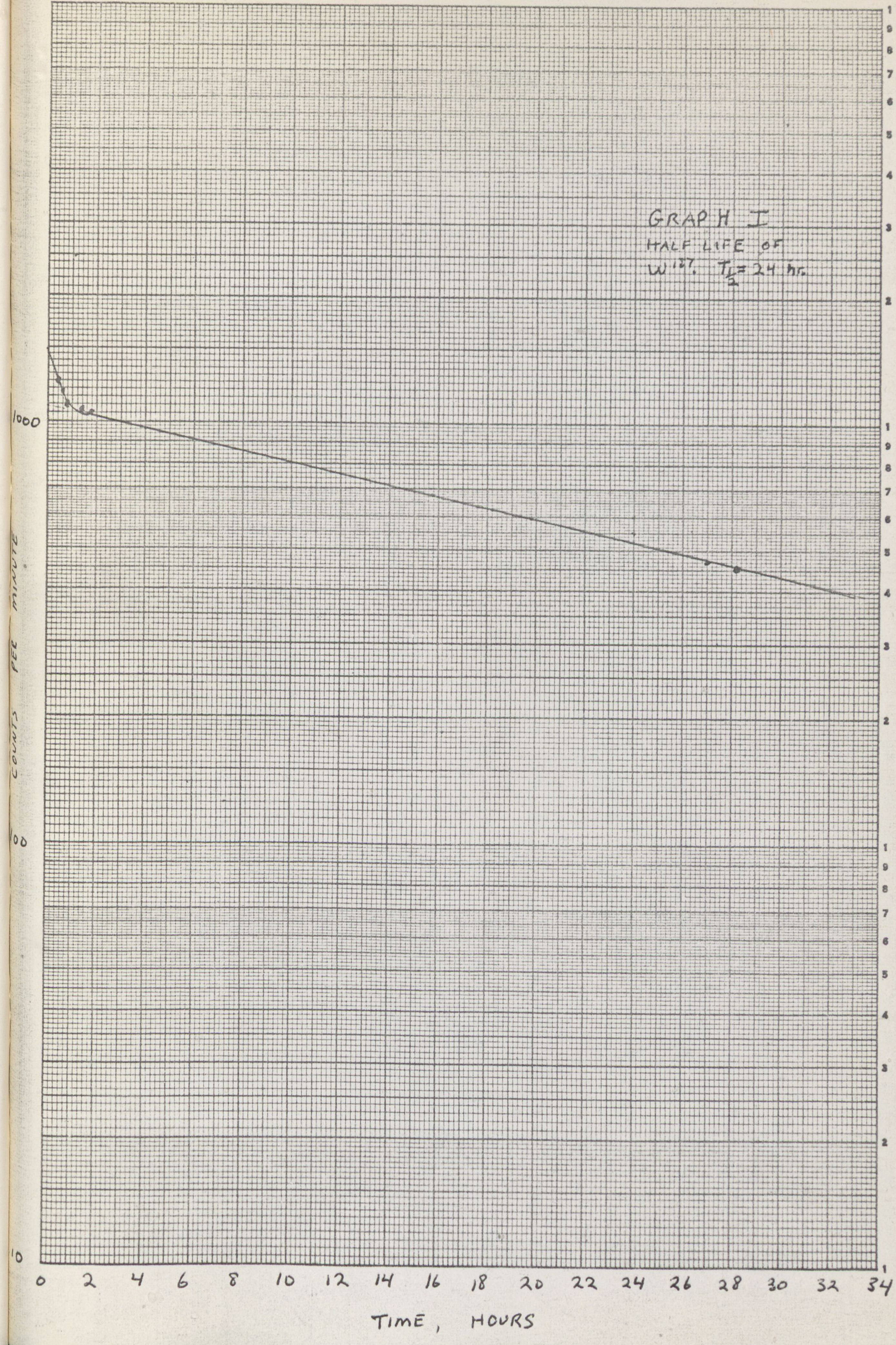
An even better way would be to precipitate on the molybdenum in the presence of tungsten. However, this method will call for further research.

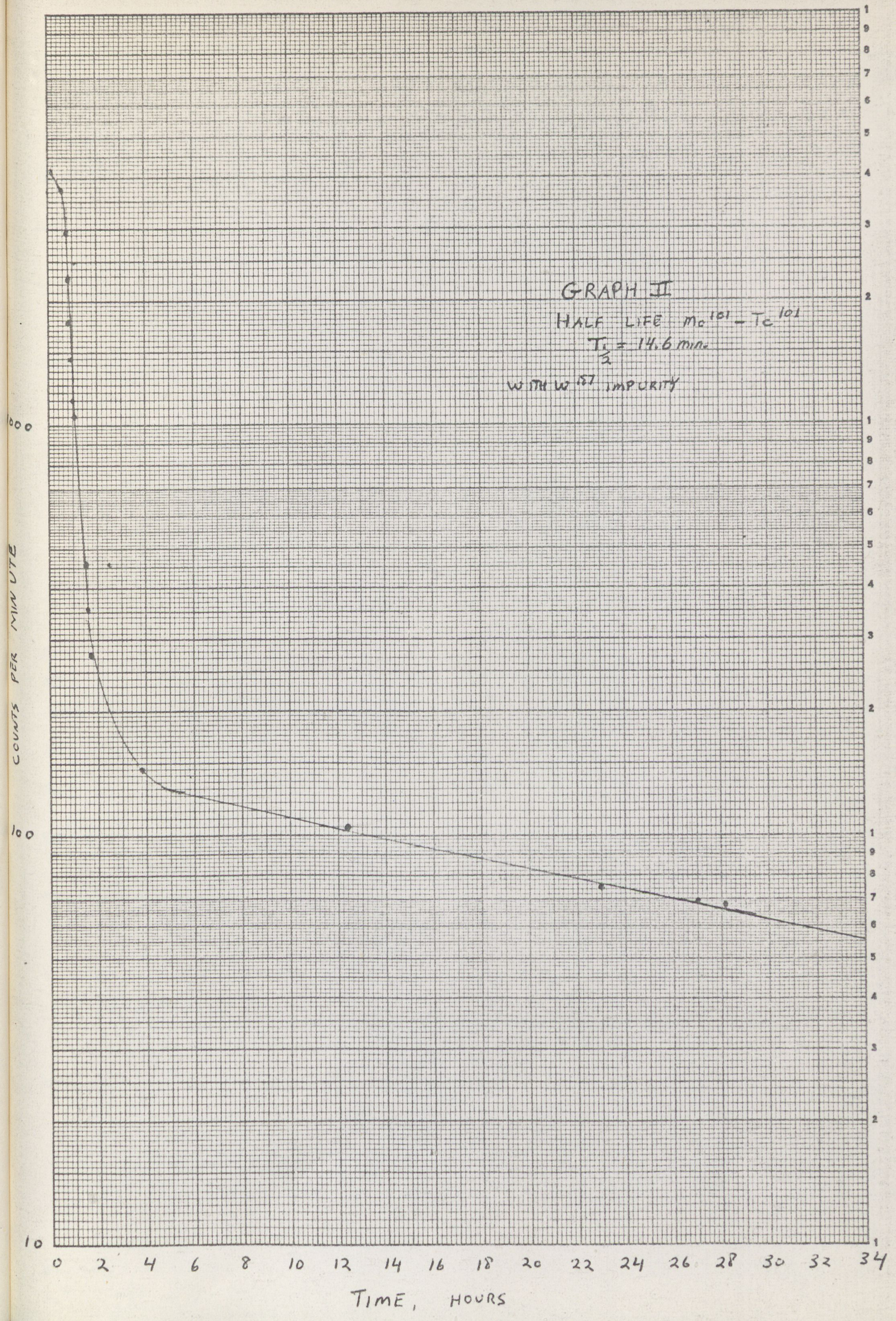
From the data in Table IV it appears as if the activation analysis is more sensitive to tungsten under conditions of long irradiation and high neutron flux than to molybdenum. With the present equipment at Union College a sensitivity of 12.1 milligrams may be reached for tungstic oxide.

The use of a highly shielded proportional counter will increase the sensitivity even more.

Though the actual goal of this work has not been reached in one year, proof of the theoretical sensitivity and expected active nuclides is shown. Ultimately irradiations will probably have to be done with a nuclear reactor with a 10^{12} neutron flux and at least a 24 hour irradiation. The sensitivity in this case warrants this method, a very valid method of determining concentrations of volatilized molybdic and tungstic oxides.

APPENDIX


GRAPH I
HALF LIFE OF
W^{127}. $T_{\frac{1}{2}}$ = 24 hr.
1000
100
10
COUNTS PER MINUTE
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
TIME, HOURS

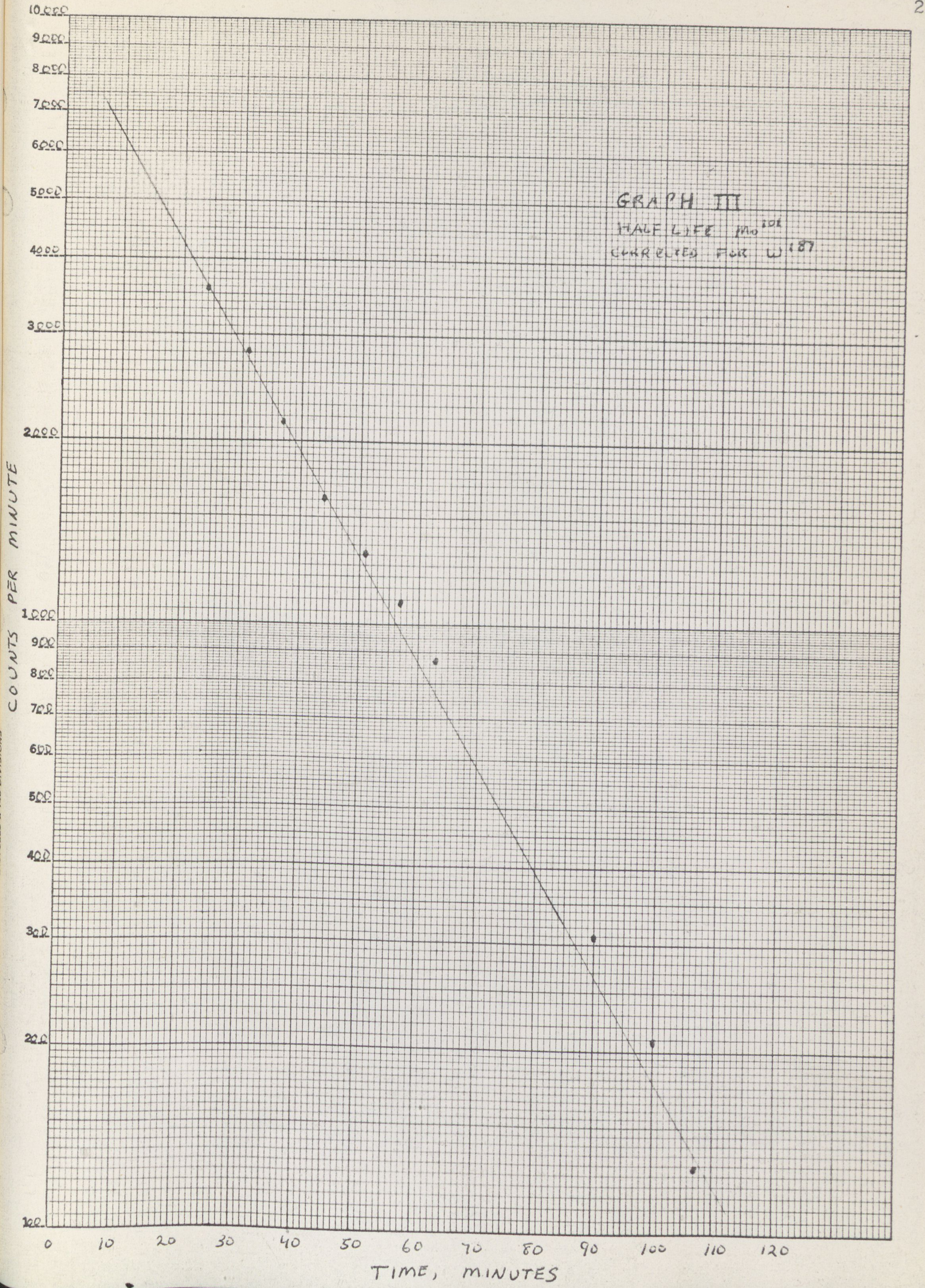


GRAPH II

HALF LIFE $Mo^{101} - Tc^{101}$

$T_{\frac{1}{2}} = 14.6$ min.

WITH W^{187} IMPURITY



GRAPH III
HALF LIFE Mo^{101}
CORRECTED FOR W^{187}

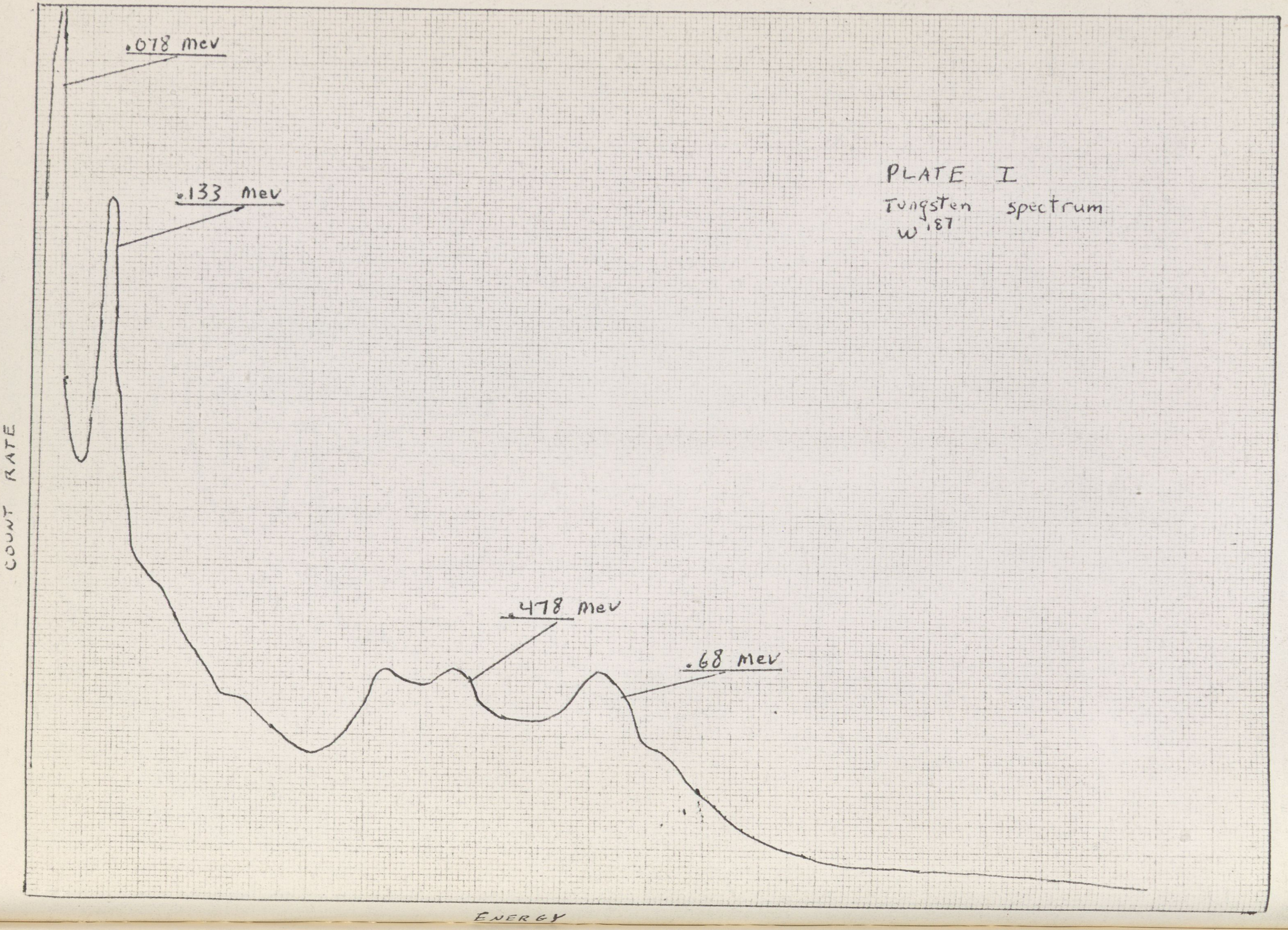


PLATE I

Tungsten spectrum

W^{187}

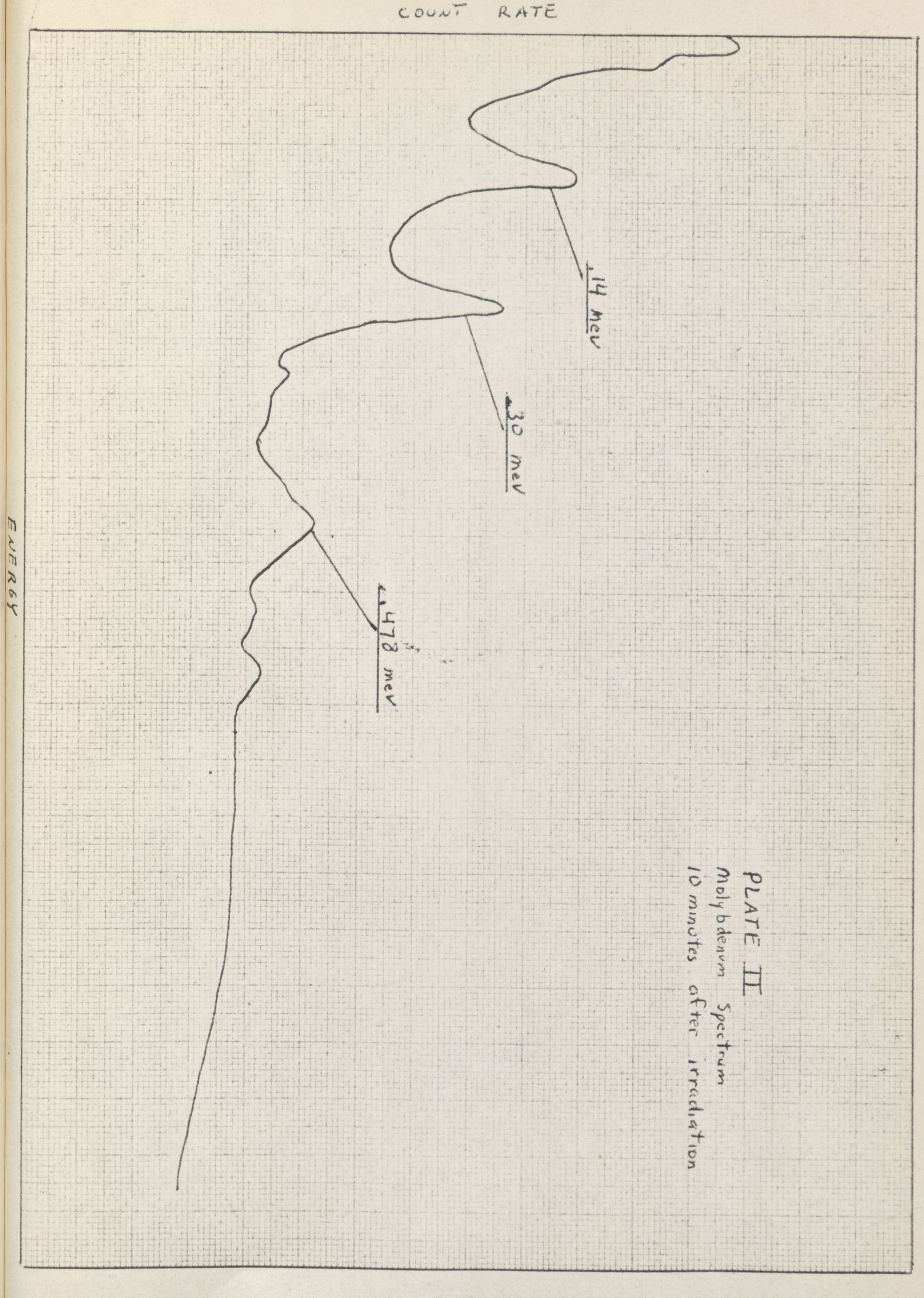


PLATE II
Molybdenum Spectrum
10 minutes after irradiation

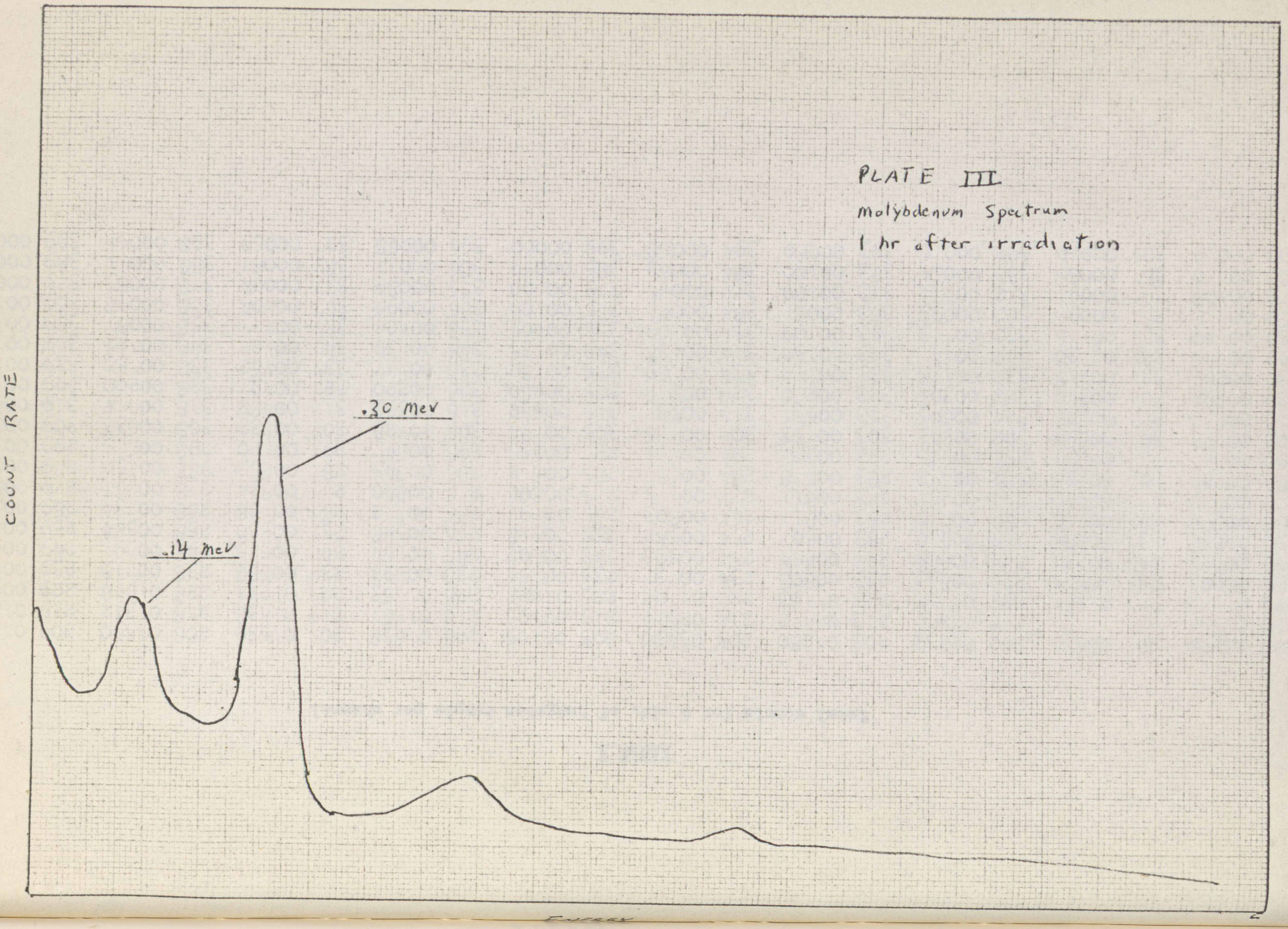


PLATE III
molybdenum Spectrum
1 hr after irradiation

TABLE VI

Total counts per channel for 4 min. of Molybdenum sample taken 10 min. after irradiation.

000	00000	001	03789	002	03852	003	03748	004	03588	005	03716	006	03400	007	03223	008	02974	009	02824
010	02779	011	02732	012	02613	013	02611	014	02537	015	02476	016	02447	017	02395	018	02460	019	02502
020	02497	021	02493	022	02620	023	02703	024	02716	025	02901	026	02966	027	02832	028	02671	029	02442
030	02347	031	02244	032	02206	033	02211	034	02067	035	02095	036	02068	037	01994	038	01992	039	01921
040	01950	041	01886	042	01904	043	01972	044	02040	045	02241	046	02395	047	02451	048	02536	049	02528
050	02440	051	02208	052	02092	053	01947	054	01713	055	01652	056	01542	057	01480	058	01375	059	01433
060	01393	061	01381	062	01462	063	01340	064	01339	065	01330	066	01344	067	01314	068	01319	069	01327
070	01335	071	01292	072	01296	073	01275	074	01251	075	01276	076	01223	077	01290	078	01292	079	01381
080	01371	081	01252	082	01306	083	01429	084	01411	085	01472	086	01515	087	01502	088	01565	089	01481
090	01548	091	01541	092	01480	093	01442	094	01444	095	01371	096	01293	097	01320	098	01307	099	01214
100	01206	101	01249	102	01215	103	01211	104	01209	105	01229	106	01199	107	01245	108	01200	109	01216
110	01147	111	01174	112	01227	113	01221	114	01256	115	01188	116	01287	117	01212	118	01171	119	01189
120	01185	121	01230	122	01212	123	01196	124	01103	125	01116	126	01170	127	01155	128	01166	129	01137
130	01103	131	01113	132	01091	133	01123	134	01053	135	01117	136	01131	137	01079	138	01139	139	01104
140	01084	141	01137	142	01088	143	01159	144	01067	145	01060	146	01081	147	01082	148	01065	149	01131
150	01098	151	01091	152	01115	153	01008	154	01064	155	01074	156	01143	157	01106	158	01070	159	01073
160	01028	161	00996	162	01034	163	01053	164	00933	165	01015	166	00922	167	00987	168	00938	169	00947
170	00970	171	00949	172	00909	173	00930	174	00922	175	00957	176	00953	177	00919	178	00957	179	00952
180	00918	181	00940	182	00926	183	00956	184	00992	185	00949	186	00985	187	00977	188	00970	189	00935
190	00931	191	00892	192	00932	193	00947	194	00924	195	00924	196	00929	197	00896	198	00960	199	00894

TABLE VII

000	00000	001	00512	002	00447	003	00464	004	00519	005	00468	006	00429	007	00415	008	00394	009	0038
010	00343	011	00397	012	00448	013	00432	014	00484	015	00487	016	00495	017	00531	018	00533	019	0051
020	00510	021	00500	022	00452	023	00478	024	00407	025	00365	026	00342	027	00314	028	00335	029	0029
030	00306	031	00308	032	00298	033	00304	034	00314	035	00309	036	00290	037	00394	038	00445	039	0057
040	00688	041	00881	042	00869	043	00818	044	00779	045	00702	046	00575	047	00439	048	00341	049	0025
050	00235	051	00180	052	00165	053	00159	054	00187	055	00143	056	00183	057	00150	058	00159	059	0017
060	00146	061	00159	062	00176	063	00140	064	00145	065	00168	066	00169	067	00135	068	00155	069	0016
070	00179	071	00152	072	00165	073	00174	074	00202	075	00174	076	00188	077	00219	078	00215	079	0022
080	00218	081	00207	082	00186	083	00189	084	00183	085	00172	086	00150	087	00175	088	00144	089	0014
090	00150	091	00154	092	00134	093	00149	094	00116	095	00126	096	00147	097	00111	098	00133	099	0013
100	00130	101	00103	102	00118	103	00123	104	00124	105	00142	106	00125	107	00131	108	00103	109	0011
110	00124	111	00093	112	00120	113	00111	114	00128	115	00124	116	00134	117	00107	118	00096	119	0012
120	00130	121	00117	122	00110	123	00121	124	00124	125	00135	126	00126	127	00114	128	00111	129	0012
130	00115	131	00111	132	00112	133	00108	134	00115	135	00113	136	00115	137	00126	138	00095	139	0011
140	00127	141	00107	142	00109	143	00108	144	00114	145	00109	146	00113	147	00104	148	00107	149	0011
150	00117	151	00110	152	00090	153	00095	154	00118	155	00124	156	00098	157	00117	158	00105	159	0010
160	00129	161	00092	162	00118	163	00119	164	00107	165	00108	166	00115	167	00090	168	00104	169	0012
170	00111	171	00112	172	00124	173	00121	174	00127	175	00106	176	00106	177	00124	178	00092	179	0009
180	00083	181	00091	182	00088	183	00080	184	00088	185	00093	186	00100	187	00074	188	00067	189	0007
190	00079	191	00074	192	00070	193	00060	194	00070	195	00049	196	00049	197	00058	198	00069	199	0006

Total counts per channel for 4 min. of molybdenum sample taken
1 hour after irradiation.

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