Submitted to Analytical Chemistry

UCRL-18979
Preprint

cy. 2

RECEIVED
LAWRENCE
RADIATION LABORATORY
OCT 9 1969
LIBRARY AND
DOCUMENTS SECTION

PREPARATION OF ISOTOPIC OXYGEN TARGETS FOR CHARGED PARTICLE ACTIVATION ANALYSIS

James F. Lamb, Diana M. Lee, and Samuel S. Markowitz

September 1969

AEC Contract No. W-7405-eng-48

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

LAWRENCE RADIATION LABORATORY
UNIVERSITY of CALIFORNIA BERKELEY

UCRL-18979 cy. 2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

PREPARATION OF ISOTOPIC OXYGEN TARGETS FOR CHARGED PARTICLE ACTIVATION ANALYSIS

James F. Lamb, Diana M. Lee, and Samuel S. Markowitz

Department of Chemistry and,
Lawrence Radiation Laboratory,
University of California,
Berkeley, California 94720

September 1969

ABSTRACT

A method has been developed for the preparation of oxygen comparison standards for charged particle activation analysis, particularly for the use of helium-3 as the activating particle, by anodic oxidation of tantalum foil. The isotopic composition of the oxide is varied by using isotopically enriched water in the electrolyte, which is 0.1 percent potassium chloride. The current passing through the cell is held constant at 40 mA while the voltage is allowed to vary. The thickness of the oxide film produced is a smooth function of time and is reproducible to within a few percent. Oxide films have been produced which vary in thickness from 0.5 mg/cm^2 for a 1 min anodization, to over 35 mg/cm^2 for an anodization time of 3 hours. The uniformity of the anodized foil and the oxygen content have been verified by helium-3 activation analysis. Standards for activation analysis may be made by this method which will reproduce any beam degradation in a sample from negligible energy loss to the complete stopping of a 10-MeV helium-3 beam. These standards have been used for isotopic oxygen analysis of several materials and for measuring excitation functions for the production of ^{19}O and ^{20}F from ^{18}O and for production of ^{18}F, ^{15}O, ^{11}C, and ^{17}F plus ^{14}O from ^{16}O.

INTRODUCTION

In 1967 Amsel and Samuel (1) reported a method for isotopic oxygen analysis of surfaces or of small amounts of oxygen containing materials based upon in-beam detection of ^{4}He-particles emitted during proton and deuteron induced reactions. Because the incident beam energy was less than about 600-keV, the method is restricted to very thin surfaces. Amounts on the order of 10^{-12}g of ^{18}O, however, can be detected. Absolute quantities of the oxygen isotopes were determined using several isotopic oxygen standards, one of which --anodic Ta_2O_5--was described as ideal for the purpose.

The relative ease of producing <u>thin</u> Ta_2O_5 films by anodic oxidation, the lack of matrix activation because of the high Coulomb barrier ($\approx$ 20 MeV) of Ta, the ability of Ta_2O_5 to withstand the increased temperature due to power deposited by the beam, and the availability of isotopically enriched H_2O which can be used in the electrolyte led us to consider the process for fabrication of targets of sufficient thickness for use in charged particle activation techniques wherein the reaction products, instead of the emitted particles are detected. These techniques may be used for bulk as well as for surface analysis.

Our particular interest has been the preparation of isotopically enriched targets which could be used for studying ^{3}He induced reactions of the oxygen isotopes at ^{3}He energies below about 30 MeV for the purpose of ^{3}He activation analysis. We describe here, in detail, the method developed for producing the Ta_2O_5 targets which we have used in studying the ^{3}He reactions of oxygen (2) and the thick Ta_2O_5 standards used for determining $^{16}O/^{18}O$ ratios in various materials (3).

ANODIZATION PROCESS

The preparation of anodic oxide films on various metals, including Ta, has been described in a book by Young (4). Vermilyea (5) has described the effect of surface pretreatment of the Ta foils, and Klerer (6) has examined anodic Ta_2O_5, finding it to be amorphous with a density of 8.0 g/cm^3 as opposed to the crystalline density of 8.7 g/cm^3. Davies, et al. (7), found that the anodization mechanism involves mobility of both tantalum and oxygen ions through the oxide film. Thompson (8) has analyzed thin Ta_2O_5 films by proton activation of natural isotopic abundance ^{18}O via the $^{18}O(p,n)^{18}F$ reaction.

Anodization of Ta is usually performed in a dilute electrolyte solution with salt or acid concentration about 0.1% by weight. The two general methods for producing oxide films of controlled thickness are (a) the constant voltage method, in which the applied potential is held constant while the current decreases as the oxide film thickens, and (b) the constant current method, in which the voltage is increased to increase the oxide thickness. In the constant voltage method, production of thick coatings is impractical because the rate of oxidation is very low at low currents. In the constant current method, the thickness of the oxide film is said to be proportional to the applied voltage reached (16 Å/V (9)), limited by electrical breakdown. Young (4) describes the limiting voltage as being characterized by sparking, oxygen evolution, and the formation of a thick discolored film. The thin films, up to a few thousand Ångstroms, are highly colored, the color having been used as a measure of the film thickness.

Our method for obtaining thick oxide coatings is based upon the experimental observation that, under our constant current conditions, the applied voltage does not continue to rise substantially after the first appearance of sparking, nor does it remain for more than a few minutes at a potential sufficient for sparking. The films produced are not spark-damaged enough to seriously affect their uniformity with respect to a 1/4-inch collimated ion beam, and the times of long anodization produce targets which are of almost any thickness desired. They appear quite uniform.

APPARATUS USED FOR ANODIZATION

The anodization cell used for the production of the thick Ta_2O_5 films, shown in Figure 1, consists of an aluminum anode plate into which is fitted the Ta foil, a teflon cell body, and a teflon cap which also serves as a bearing for the revolving platinum cathode. The lower end of the cathode is a 5/8-inch diameter platinum disc which just clears the walls of the 3/4-inch bore cell body. The reflux condenser, fitted into the side of the cell body, minimizes evaporative losses in the 0.1% KCl electrolyte which may be prepared from isotopically enriched H_2O. The revolving cathode and the Ta foil anode, positioned 0.5 cm apart, are connected across a 0 - 500 V-DC power supply with an ammeter and voltmeter in the external circuit.

ANODIZATION PROCEDURE

High purity tantalum anodes (99.9% Ta) were cut from 0.002-inch thick foil and degreased with acetone. Surface scratches were removed by chemical polishing in a solution containing 5 parts H_2SO_4, 2 parts HNO_3, and 1.5 parts HF by volume of the concentrated acids.

The assembled anodization cell was placed on an asbestos insulated hot plate, 4 ml of 0.1% KCl electrolyte introduced through the condenser bore, and the cathode adjusted to revolve at about 300 rpm. The temperature of the electrolyte was raised to boiling immediately before beginning the anodization, and then the hot plate was turned off. During anodization the power deposited in the cell maintained the temperature of the electrolyte at the boiling point. An air stream directed at the cell base served to carry off excess power deposit heating.

The anodization process was begun by adjusting the current, as rapidly as possible, to its constant value of 40 mA where it was maintained by manually adjusting the potential. The behavior of the applied potential during an anodization period of 160 minutes is shown in Figure 2. At about 380 volts, reached after about 3 minutes of anodization, sparking is first observed. These sparks appear as tiny points of light distributed over the surface of the oxide film. Within the next 4 minutes the potential passes through a maximum value and begins to decrease. Sparking is observed until the potential has fallen to about 380 volts. Ta foils which are removed from the cell at times corresponding to the sparking potential range are gray in color with tiny white spots distributed randomly over the surface. After about 15 minutes of plating the oxide films are completely white and appear uniform to visual inspection. At the end of the 160 minute anodization the volume of the remaining electrolyte was found to be within 0.2 ml of the original 4-ml volume. (Much of this loss is due to incomplete mechanical recovery of the electrolyte from the cell.)

Eighteen anodizations were carried out using the above procedure with plating times of 1 minute to 160 minutes. The mg thickness of the oxide films were determined by the increases in weight of the Ta foils. The results are shown in Figure 3. It must be noted that the abscissa of the figure represents the mg thickness of the oxygen incorporated into the Ta surface. Ta_2O_5 is about 18% oxygen so that the thickest oxide coating shown, after anodization for 160 minutes, is about 39.1 mg/cm^2 Ta_2O_5. Based upon the 8.0 mg/cm^3 density, this corresponds to a film thickness of almost 0.005 cm.

The reproducibility of the process has been established by the preparation of about one hundred Ta_2O_5 targets during the course of our work on ^{3}He activation analysis. Under the conditions specified the mg thickness of the oxygen anodized into the Ta foils during given plating times may be determined from the film thickness vs. time curve to within about 0.1 mg/cm^2.

FILM UNIFORMITY - ^{3}He ACTIVATION

That the targets prepared were sufficiently uniform for use as oxygen standards was demonstrated by ^{3}He activation analysis. The most convenient method for testing uniformity would be activation analysis of a large number of foils of different thicknesses at the same reaction cross section and under identical counting conditions. Deviations from a linear plot of activity per unit beam intensity vs. weight of oxygen on the anodized foils could be interpreted as nonuniformity in the films. Such a procedure is complicated because the reaction cross section is a function of beam energy which is, in turn, a function of the thickness of target material traversed by the beam. This may be accounted for by calculating the energy degradation in the incident ion beam from the range energy curve, Figure 4, and then

determining an average reaction cross section over this energy interval from the reaction excitation function, Figure 5. The range-energy curve shown was calculated using the computer code of Steward (10), and the excitation function was taken from Markowitz and Mahony (11).

The results of such a procedure are shown in Figure 6. The anodized foils were individually bombarded for 10 seconds each with 10-MeV $^{3}He^{++}$ ions at the Berkeley heavy ion linear accelerator at a beam current of about 0.2 μA. Recoil losses were prevented by thin gold cover foils. The positron decay of the 110 minute ^{18}F activity induced in each target was followed by counting the 511-keV annihilation radiation using a NaI(Tl) detector coupled to a multichannel analyzer. The ^{18}F activity resulting from activation of pre-existing oxides in the high purity Ta and Au foils was accounted for by irradiating an unanodized target blank. The dashed line in the figure represents the maximum obtainable activity which could result from activation of a target thick compared to the range of the ion beam under the above bombardment conditions, as calculated from the average cross section.

CONCLUSION

Anodic oxidation of high purity Ta foil can be used to produce targets and standards for oxygen analysis by charged particle activation. By using ^{18}O isotopically enriched H_2O in the preparation of the electrolyte, isotopic oxygen targets can be inexpensively produced. The consumption of the electrolyte during the process is less than 0.2 ml for the production of an oxide film whose thickness is about 39 mg/cm^2 Ta_2O_5.

Ta_2O_5 films may be prepared to within 0.1 mg/cm^2 of the desired oxygen thickness. With this high degree of reproducibility the degrading power of a sample of any material can be adequately matched by the oxygen standard. Such a matching of effective thicknesses can reduce the analytical calculations to the simple ratio of the activities induced in the sample and standard.

The thickest oxide films produced in this work are sufficient to completely stop an incident 10-MeV ^{3}He ion beam. Although we have not continued the anodization beyond the times shown in the figures, the data do not indicate the approach to any thickness limitation.

The explanation for the rather interesting shape of the voltage curve in Figure 2 and the mechanism of the process remain to be explored.

Work performed under the auspices of the U. S. Atomic Energy Commission

LITERATURE CITED

(1) G. Amsel and D. Samuel, Anal. Chem., 39, 1689 (1967).

(2) D. M. Lee, J. F. Lamb, and S. S. Markowitz, Lawrence Radiation Laboratory Report UCRL-17989, 10 (1967).

(3) J. F. Lamb, D. M. Lee, and S. S. Markowitz, Proc. of the 2nd Conf. on Practical Aspects of Activation Analysis with Charged Particles, Liege, Belgium, 1967, 225 (1968).

(4) L. Young, "Anodic Oxide Films", Academic Press, New York, 1963.

(5) D. A. Vermilyea, J. Electrochem. Soc., 110(4), 250 (1963).

(6) J. Klerer, J. Electrochem. Soc., 112(9), 896 (1965).

(7) J. A. Davies, B. Domeij, P. P. S. Pringle, and F. Brown, J. Electrochem. Soc. 112(7), 675 (1965).

(8) B. A. Thompson, Anal. Chem., 33, 585 (1961).

(9) D. A. Vermilyea, J. Electrochem. Soc., 102, 655 (1955).

(10) P. G. Steward, Lawrence Radiation Laboratory Report UCRL-18127, (Ph.D. Thesis), 1968.

(11) S. S. Markowitz and J. D. Mahony, Anal. Chem., 34, 329 (1962).

FIGURE CAPTIONS

Fig. 1. Electrolytic cell for anodization of Ta foils at the electrolyte boiling point, ≈ 100°C.

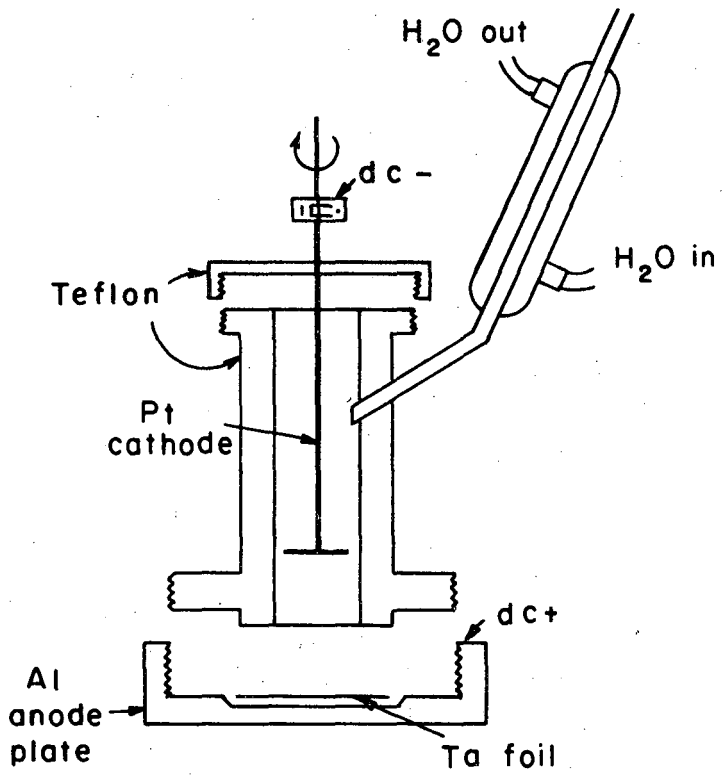
Fig. 2. Variation in the applied voltage during boiling point anodization of Ta foil. Current = 40 mA, temperature ≈ 100°C.

Fig. 3. Thickness of oxide coating produced by anodization of Ta foils in 0.1% KCl. Current = 40 mA, temperature ≈ 100°C.

Fig. 4. Ranges of ^{3}He ions in Ta_2O_5. The ranges were calculated using the computer code of Steward (9).

Fig. 5. Excitation function for production of ^{18}F from ^{16}O by ^{3}He ion bombardment, (Ref. 10).

Fig. 6. Activation of ^{16}O in the Ta_2O_5 films by the $^{16}O(^{3}He,p \text{ and } n)^{18}F$ reaction using 10-MeV $^{3}He^{++}$ ions. The dashed line represents the approximate thick target activity normalized to 10 MeV.



XBL671-345

Fig. 1.

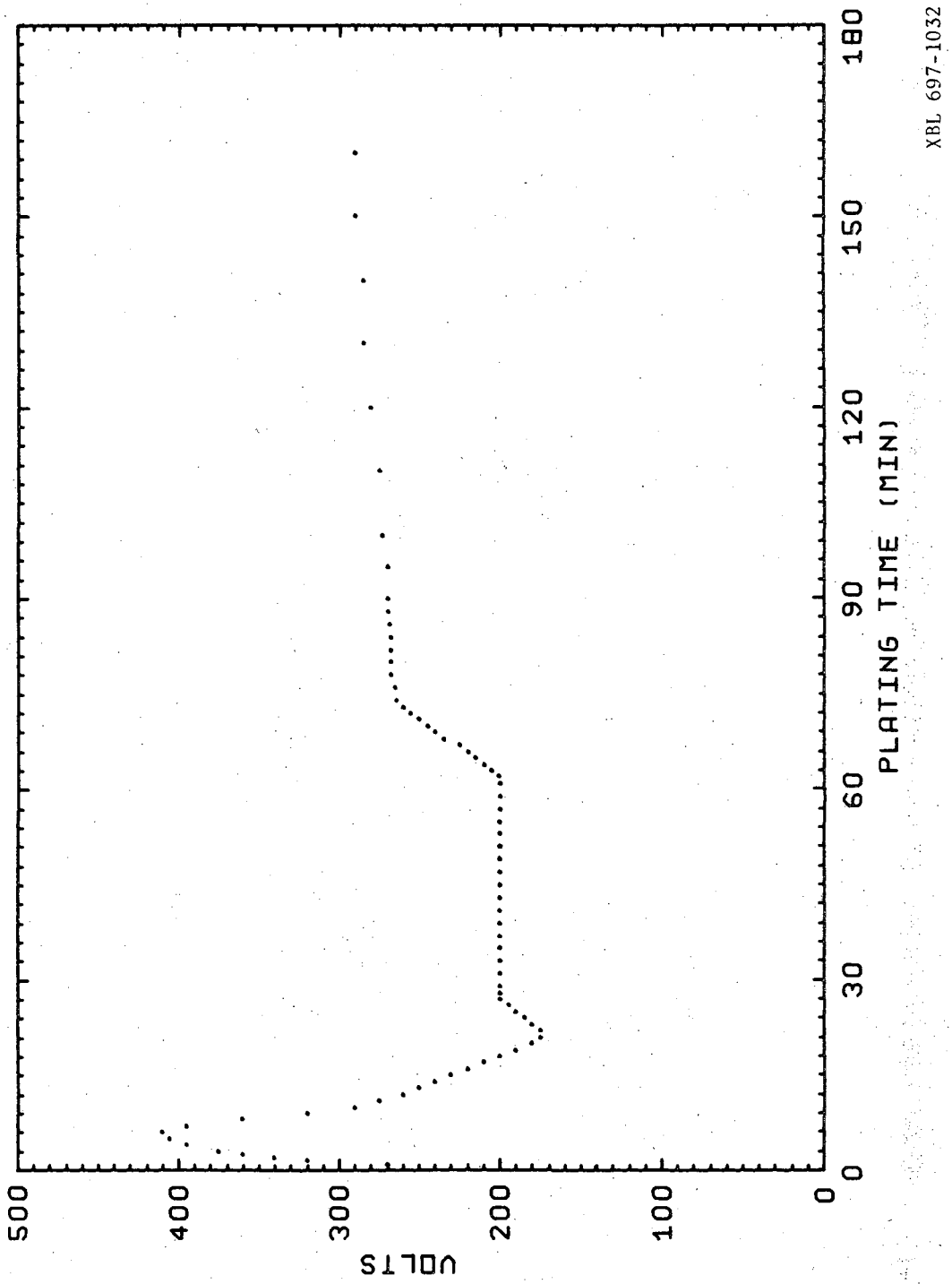

VOLTS
500
400
300
200
100
0
0
30
60
90
120
150
180
PLATING TIME (MIN)
XBL 697-1032

Fig. 2.

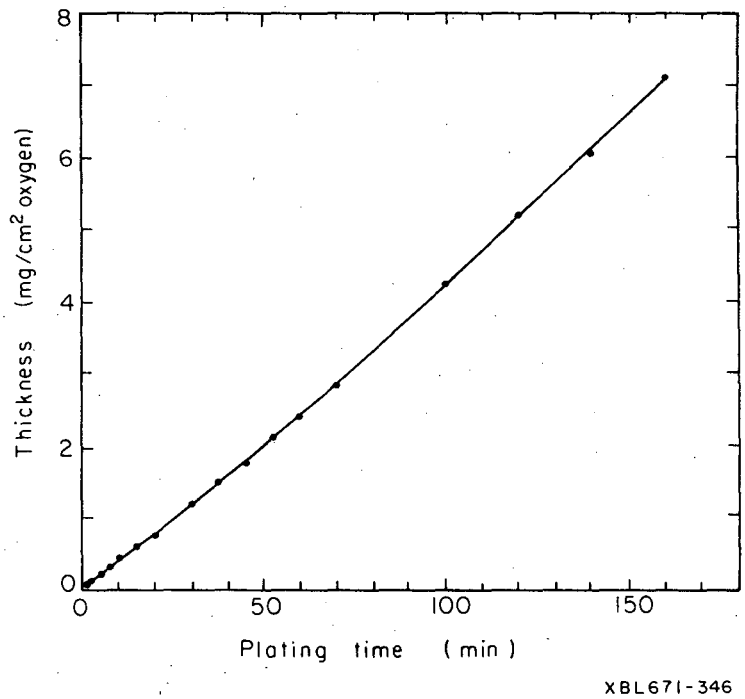
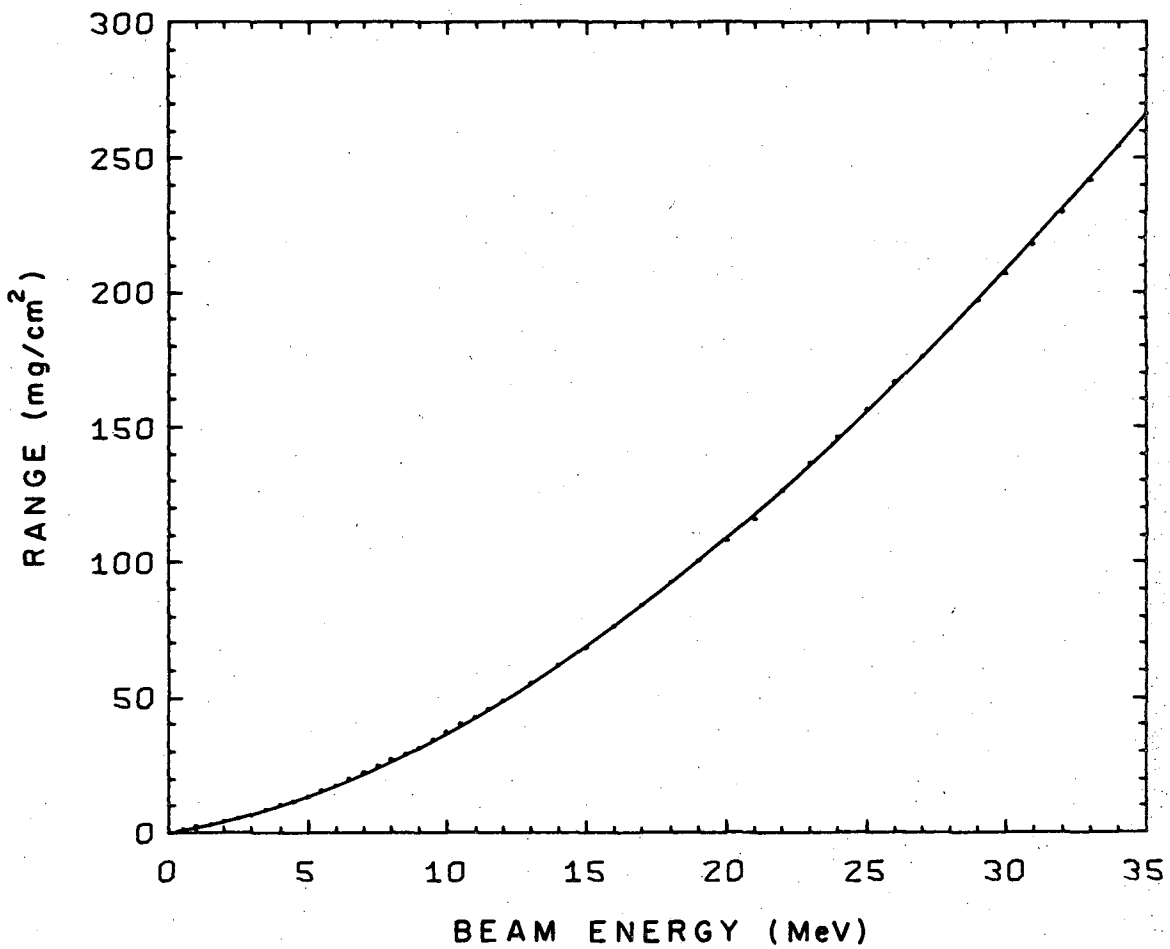
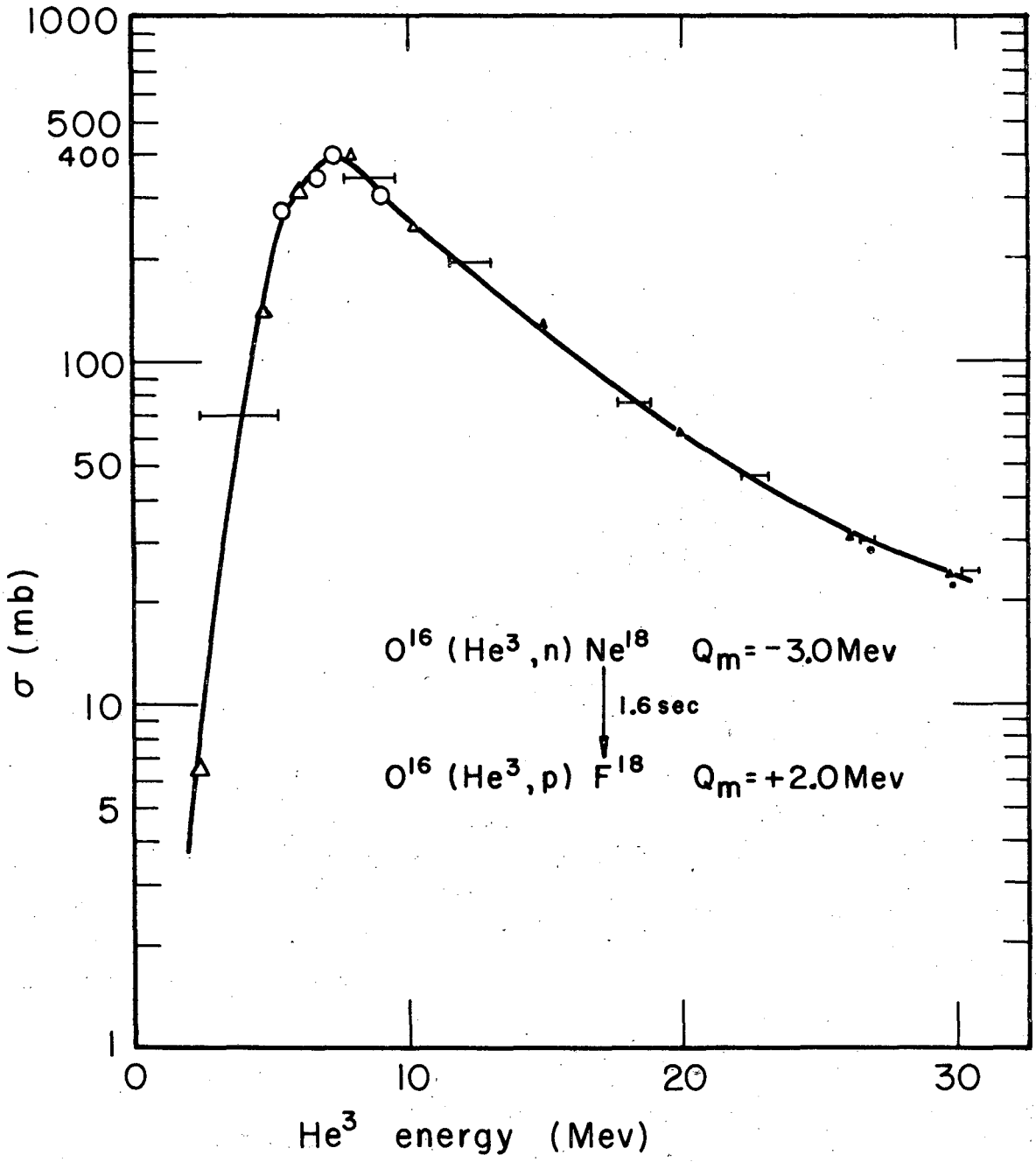

8
6
4
2
0
Thickness (mg/cm² oxygen)
0
50
100
150
Plating time (min)
XBL671-346

Fig. 3.



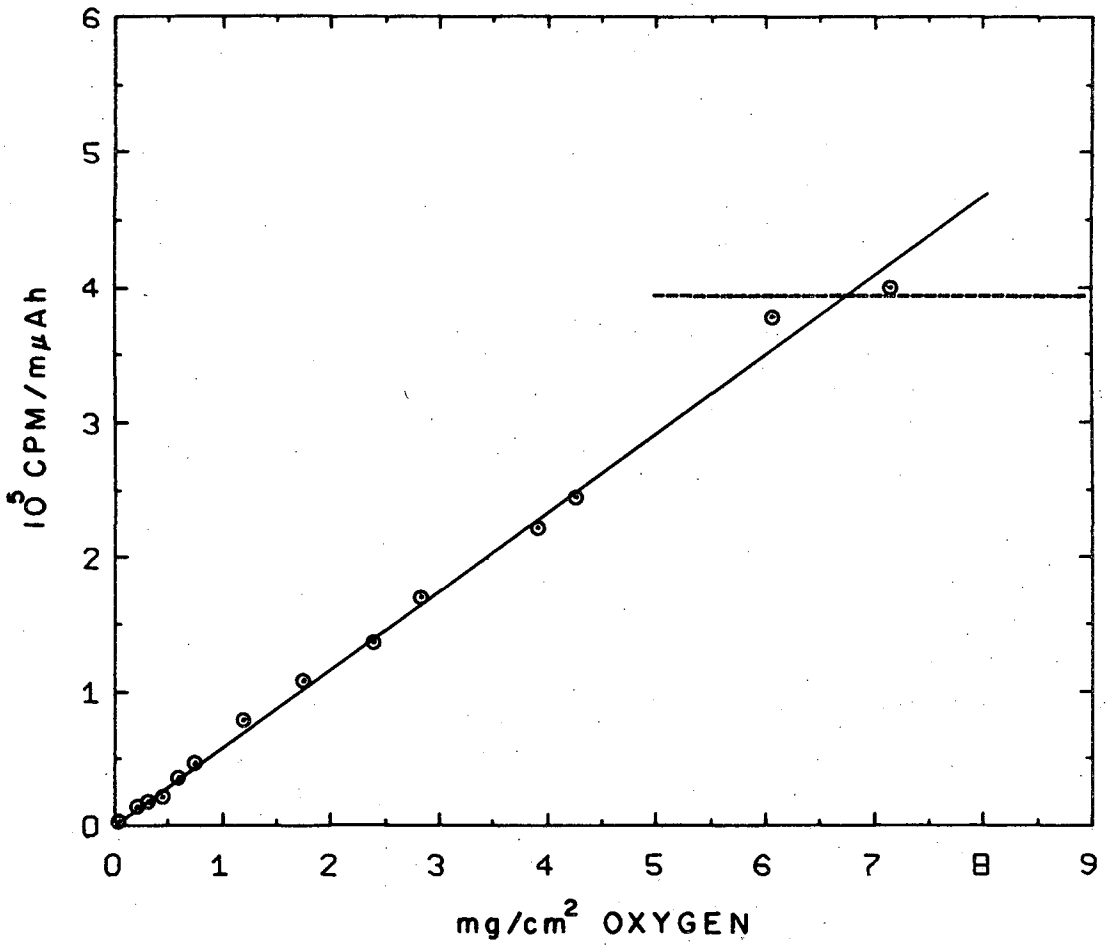
XBL 698-1246

Fig. 4.



MU-24829

Fig. 5.



XBL 698-1276

Fig. 6.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

TECHNICAL INFORMATION DIVISION
LAWRENCE RADIATION LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720