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**SOME APPLICATIONS OF X-RAY FLUORESCENCE SPECTROGRAPHY
TO THE DETERMINATION OF URANIUM AND THORIUM**

CRDC-843

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SOME APPLICATIONS OF X-RAY FLUORESCENCE SPECTROGRAPHY
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ABSTRACT

Several methods for the determination of uranium and thorium by X-ray fluorescence spectrography are described. In pure solutions the sensitivity for these elements is 5 - 10 ppm. For solutions containing gross concentrations of impurities, strontium is added as an internal standard. Precision and accuracy of the determinations are about 1% when working in the optimum concentration range.

INTRODUCTION

A laboratory engaged in the analysis of uranium and thorium-bearing mixtures may encounter a wide variety of samples that contain a number of interfering cations or anions. Spectrophotometric methods prove successful in many instances but are often subject to interferences unless separations are carried out.

X-ray fluorescence methods, because of their speed and greater freedom from interference, are often superior for handling many types of samples. A considerable number of papers have appeared in the literature in recent years on X-ray fluorescence analysis of uranium and thorium. They cover a wide variety of applications from solutions (3,6,7,9,14) to complicated mineral mixtures (1,4,5,8,11). In almost all cases the speed and ease of analysis has been emphasized.

This report describes several applications of X-ray fluorescence methods for uranium and thorium analysis which are in use on the Chalk River project. The methods described can readily be modified to cover most types of samples that are likely to be encountered.

INSTRUMENTATION

A Philips, 3-specimen X-ray fluorescence spectrograph, model 52254, was used in this work. Philips FA-60, molybdenum and tungsten target, X-ray tubes were employed. The fluorescent beam was diffracted by a LiF crystal ($2d = 4.028\text{\AA}$). Collimators

were: primary - 1/8 in. parallel plate, secondary - 0.005 in. x 4 in. parallel plate. A Philips, type 52245, scintillation counter was used as a detector in conjunction with an Atomic Instrument Company, model 510, single-channel pulse-height analyzer.

DETERMINATION OF URANIUM

1. Determination of Uranium in Nitric Acid Solution

Calibration curves for the determination of uranium in dilute nitric acid were prepared using both tungsten and molybdenum target X-ray tubes. It was known that the sensitivity for uranium was considerable higher with a molybdenum target (14), but it was considered desirable to be able to carry out the determination using either tube.

Uranium standards were prepared by dissolving high-purity U_3O_8 in nitric acid and diluting to the desired concentrations. An arbitrary sample volume of 10 ml was used. This could be reduced to 5 ml if required. Solutions were made approximately 1N in nitric acid since it was found that in solutions with no free acid the uranium tended to precipitate during the sample irradiation. No difficulty occurred with dilute acid solutions.

Calibration curves extending up to 1mg U/ml were obtained at two different power levels for both X-ray tubes, namely: 50 kvp - 50 ma and 40 kvp-40 ma. These are shown in Figures 1 and 2. All measurements were made on the uranium $L\alpha$ line (nominal 2θ value, 26.14°). Samples were counted in

duplicate, a minimum of 128,000 counts being recorded. A 1N nitric acid solution served as a blank to correct for background. The pulse-height analyzer was used to help reduce the high background of scattered radiation.

A comparison was made between results obtained by the X-ray fluorescence method and the spectrophotometric thiocyanate method on uranium solutions containing only minor amounts of other elements. Results are shown in Table I.

Table I

Determination of Uranium in Solution
Comparison of Chemical and X-ray Results.

<u>Sample No.</u>	<u>Uranium conc. (mg/ml)</u>	
	<u>Chem. anal.</u> <u>(thiocyanate method)</u>	<u>X-ray anal.</u> <u>(ave. of 6 determinations) *</u>
ES 9	303	310
ES 10	344	346
ES 11	90	85.2
DM 26	310	312
"standard"	460	461

* The calculated standard deviation for the uranium determination was about 1% of the amount present.

2. Determination of Uranium in the Presence of Impurities -
Internal Standard Technique

The direct determination of uranium cannot be carried out in the presence of large amounts of impurities. The amount

of impurity that can be tolerated depends on the atomic number of the element since the interference is essentially caused by absorption effects. This interference is at a minimum in the dilute solutions used, but becomes significant when the impurities exceed the concentration of the uranium. It was established that the following weight ratios of impurity element to uranium gave about a 1% error in the uranium determination: $Al/U = 10$, $Fe/U = 3$, $Th/U = 1$.

By using the internal standard technique, much higher impurity levels can be tolerated. This technique has been described elsewhere (2,13) and there are certain rules which must be observed in choosing an element for this purpose⁽⁵⁾. Fish and Huffman⁽¹⁰⁾, and Silverman, Houck and Moudy⁽¹²⁾ have described specific methods of uranium analysis in solutions using the internal standard technique.

Two possibilities were considered here for uranium analysis: strontium and yttrium. Strontium proved to be the more satisfactory for general use. Yttrium was acceptable in the absence of thorium. The thorium $L_{\beta 6}$ line interferes with the yttrium K_{α} line and hence the yttrium/uranium intensity ratio varies with thorium concentration.

The standard strontium solution was prepared by dissolving 2.5 grams of reagent grade strontium nitrate in water and diluting to 500 ml. Strontium solution, 2 ml, was added to the uranium sample aliquot before diluting to the 10 ml volume.

A series of uranium standards was prepared to give solutions ranging in concentration up to 1 mg U/ml. Strontium was added and a calibration curve prepared from the U/Sr ratios calculated from the counting data. Total counts of 256,000 were obtained for both the uranium L_{α} and strontium K_{α} lines. A background count was taken at $2\theta = 30.00^{\circ}$. The resulting curve is shown in Figure 3.

Table II shows a comparison of results obtained by this method with chemical analysis results for a group of aluminum-thorium-uranium alloys.

Table II

Determination of Uranium in Al-Th-U Alloys
Using Sr as Internal Standard,
Comparison of Chemical and X-ray Results.

<u>Sample No.</u>	<u>Wt. % U.</u>	
	<u>Chem. anal.</u> <u>(thiocyanate Method)</u>	<u>X-ray anal.</u>
19	1.60	1.65
20	1.70	1.72
21	1.21	1.24
22	1.20	1.24
23	0.63	0.59
24	0.64	0.61

Agreement between the results is quite good considering the nature of the samples and the low levels of uranium being determined. The average difference between chemical and X-ray results is only 0.03% uranium.

3. Determination of Uranium in Organic Solutions

The feasibility of the direct determination of uranium in organic solutions was investigated briefly. "Soltrol" - 20% tributyl phosphate was taken as being a typical system. A chemically analyzed solution of uranium in TBP-Soltrol was used as a standard. Appropriate aliquots were diluted with solvent, and 10 ml samples measured as was done for the aqueous solutions. The curves obtained for 50 kvp - 50 ma and 40 kvp - 40 ma are shown in Figure 4. It will be noted that the sensitivity in this medium is considerably greater than the sensitivity in aqueous solutions. This is because the solvent system is a lighter matrix than the aqueous solutions.

4. Determination of Uranium in UO₂ - ThO₂ Mixtures

Since a number of samples of oxide mixtures are received in connection with the fuel-development program, the direct X-ray fluorescence analysis of such mixtures was considered desirable. Chemical analysis of these samples is time consuming, chiefly because of the difficulty encountered in getting them into solution. X-ray analysis obviates this difficulty.

An attempt was made to prepare standards by simple mechanical mixing of the pure oxides followed by briquetting, but this proved to be unsatisfactory. The uranium fluorescent

intensities were found to decrease gradually with increase in mixing time, and uniformity of the pellets was poor.

To circumvent this difficulty, accurately weighed mixtures of U_3O_8 and ThO_2 were dissolved in nitric acid. The uranium and thorium were then precipitated with ammonia, filtered and washed. After ignition to the mixed oxides and grinding to -325 mesh, the standards were mixed with cellulose in the proportion of four parts oxide to one part cellulose and briquetted into pellets one inch in diameter.

Figure 5 shows the calibration curve obtained using these standards, which were irradiated with a molybdenum target X-ray tube operated at 40 kvp and 40 ma. The time for 256,000 counts for the uranium L_{α} line and 64,000 counts for the background at $2\theta = 25.00^\circ$ were recorded for both sides of the briquettes, and the results averaged. The specimens were rotated during irradiation.

Unknown oxide samples are ground to -325 mesh, mixed with cellulose powder in the same proportion as the standards, briquetted and analyzed on the spectrograph.

Samples of uranium-thorium alloys can also be handled by this method by igniting them to the oxides and then proceeding as above.

DETERMINATION OF THORIUM

1. Determination of Thorium in Nitric Acid Solution

As was done for uranium, calibration curves (Figures 6 and 7) were prepared using both tungsten and molybdenum

target X-ray tubes. Standards were prepared from a pure thorium nitrate solution whose thorium concentration had been accurately determined gravimetrically. Suitable dilutions were made from this stock solution, and 10 ml samples were irradiated at 50 kvp - 50 ma and 40 kvp - 40 ma. Duplicate counting times of at least 128,000 counts were measured for the thorium L_{α} line (nominal 2θ value, 27.46°). Samples were made about 1N in nitric acid and a background correction was made using 1N nitric acid as a blank. The sensitivity of the thorium determination is about the same as for uranium. i.e. about 5 - 10 ppm in a relatively pure solution.

2. Determination of Thorium in the Presence of Impurities - Internal Standard Technique.

Among the elements that have been used as an internal standard in the X-ray spectrometric determination of thorium are selenium, thallium, strontium and bromine. Strontium was selected for this work since it had already been selected for the uranium determination.

A calibration curve was obtained in an analogous manner to the uranium determination, and is shown in Figure 8. Table III compares results obtained by this method with gravimetric thorium determinations on a group of Th-Al alloys.

Table III

Determination of Thorium Using an Internal Standard,
Comparison of Chemical and X-ray Results.

<u>Sample No.</u>	<u>Wt. % Th</u>	
	<u>Chem. Anal. (gravimetric)</u>	<u>X-ray</u>
T-1	26.48	26.3
T-1A	28.18	27.8
T-2A	27.17	26.5
T-2	28.12	27.7
B-2	31.17	31.4
B-1	31.02	30.6

CONCLUSIONS

Several X-ray spectrometric methods have been developed for routine determination of uranium and thorium. The methods are comparable to spectrophotometric procedures in sensitivity and accuracy. In a number of applications the X-ray method is notably superior in speed and in its freedom from interference.

The X-ray methods outlined in this report are not intended to cover all possibilities, but rather to give a general idea of the usefulness of the technique. Procedures for specific applications should require only a small amount of experimental effort.

LITERATURE CITED

- (1) Adler, I. and Axelrod, J.M., Anal. Chem 27, 1002 (1955)
- (2) Adler, I. and Axelrod, J.M., Spectrochim. Acta 7, 91 (1955)
- (3) Birks, L.S. and Brooks, E.J., Anal. Chem. 23, 707 (1951)
- (4) Campbell, W.J. and Carl, H.F. Anal. Chem. 27, 1884 (1955)
- (5) Cope, J.H., Norelco Reporter 3, 41 (1956)
- (6) Flikkema, D.S., Larsen, R.P., and Schablaske, R.V.,
U.S. Atomic Energy Commission Rept. No. ANL-5641
- (7) Kehl, W.L. and Russel, R.G., Anal. Chem 28, 1350 (1956)
- (8) King, A.G. and Dunton, P., Science 122, 72 (1955)
- (9) Moak, W.D. and Pojasek, W.J., U.S. Atomic Energy Commission
Rept. No. KAPL-1879
- (10) Fish, G. and Huffman, A.A., Anal. Chem. 27, 1875 (1955)
- (11) Salmon, M.L. and Blackledge, J.P., Denver Research Institute
Publication: "Analysis of Uranium Minerals by X-ray
Spectrography" - Sept. 13, 1954.
- (12) Silverman, L., Houck, W.W. and Moudy, L., Anal. Chem.
29, 1762 (1957)
- (13) Von Hevesy, G.: "Chemical Analysis by X-rays and its
Applications" McGraw Hill Book Company, Inc., New York
(1932)
- (14) Wilson, H.M., and Wheeler, G.V., U.S. Atomic Energy
Commission Rept. No. IDO-14393

FIGURE I
DETERMINATION OF URANIUM IN HNO₃ SOLUTION

50 KVP - 50 MA

▽ - Mo TARGET
○ - W TARGET

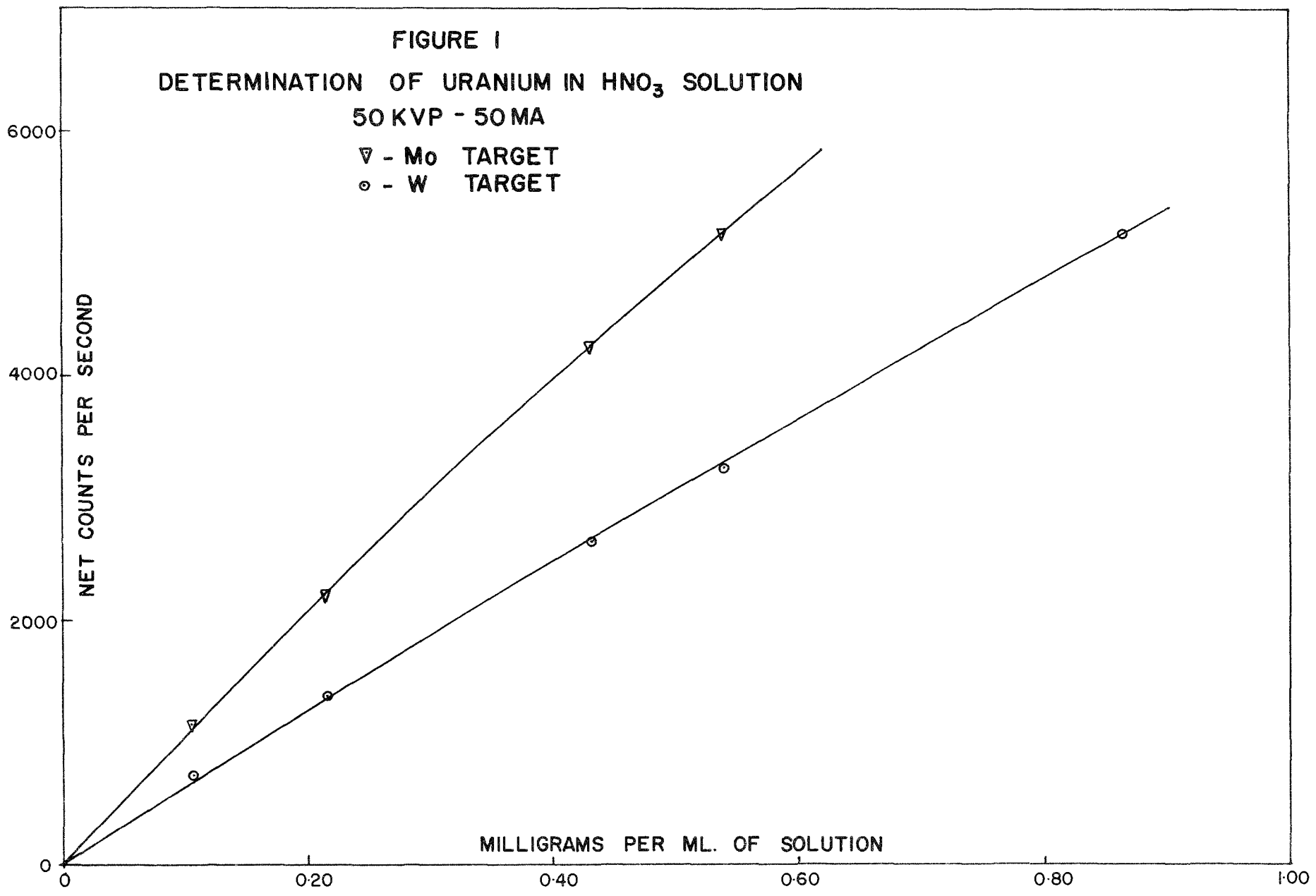


FIGURE 2
DETERMINATION OF URANIUM IN HNO₃ SOLUTION
40KVP - 40MA
▽ - Mo TARGET
○ - W TARGET

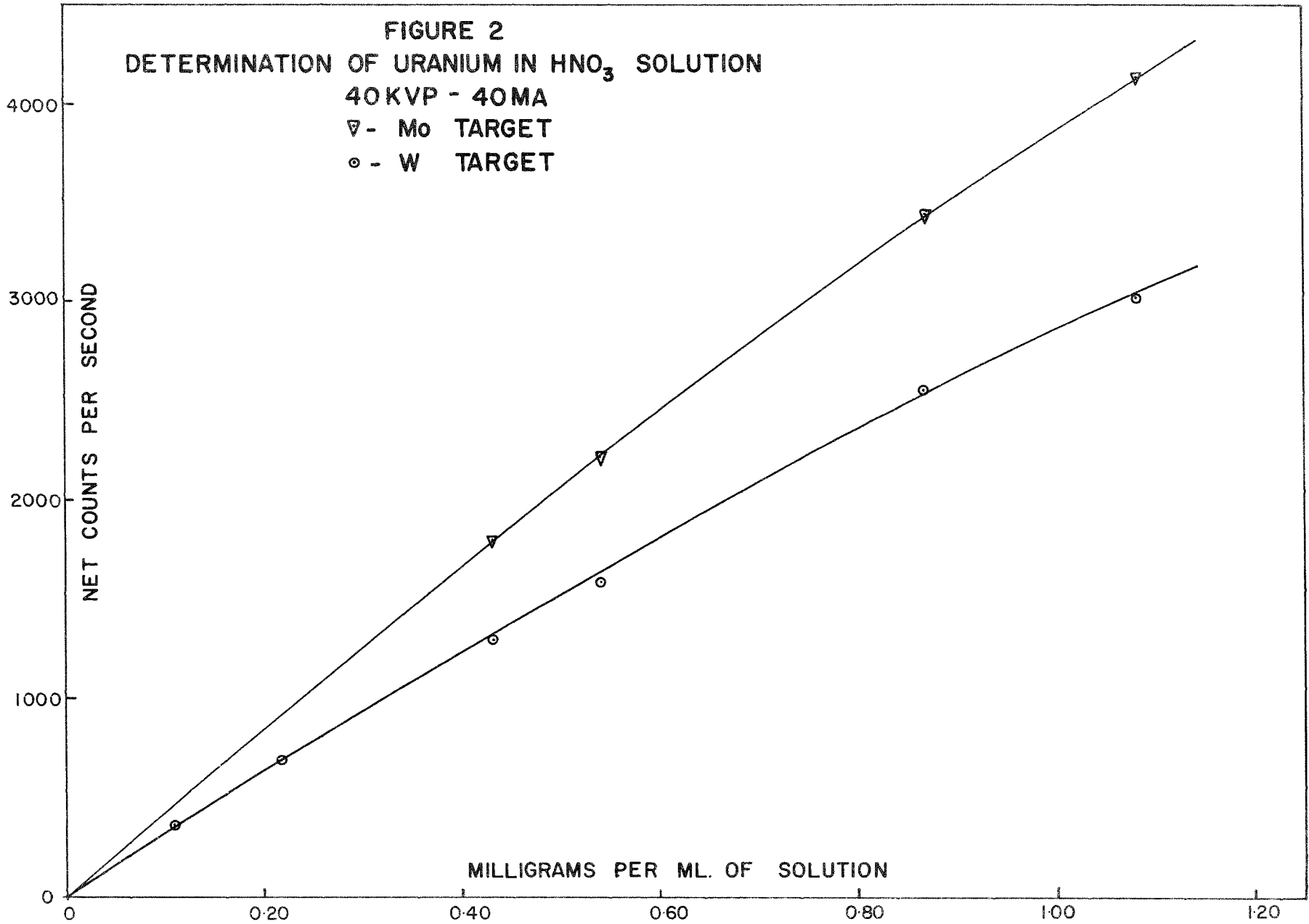


FIGURE 3
DETERMINATION OF URANIUM IN AQUEOUS SOLUTION
USING STRONTIUM AS AN INTERNAL STANDARD
▽ - Mo TARGET
○ - W TARGET

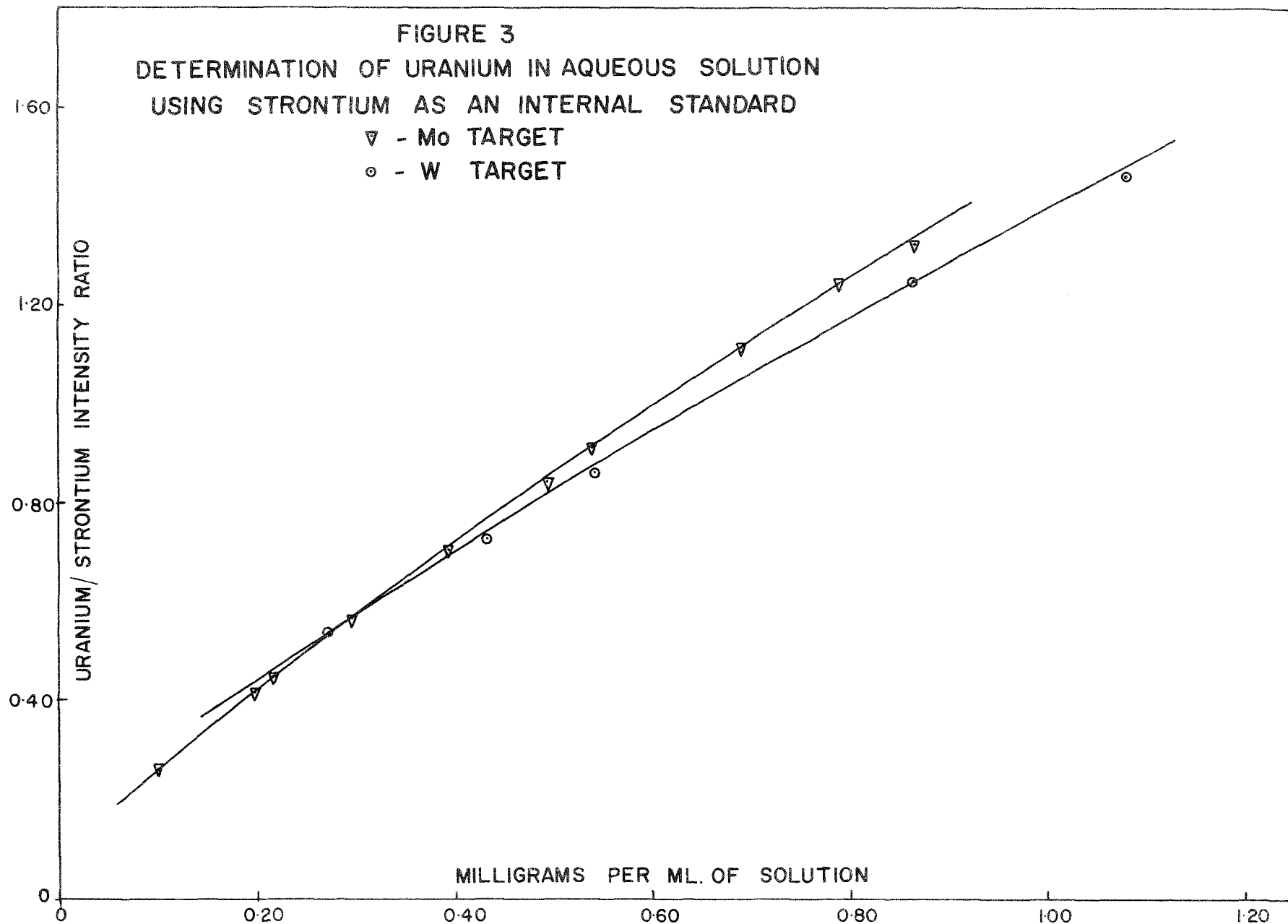


FIGURE 4
DETERMINATION OF URANIUM IN 20% TBP-SOLTRON
Mo TARGET

▽ - 50KVP - 50MA

○ - 40KVP - 40MA

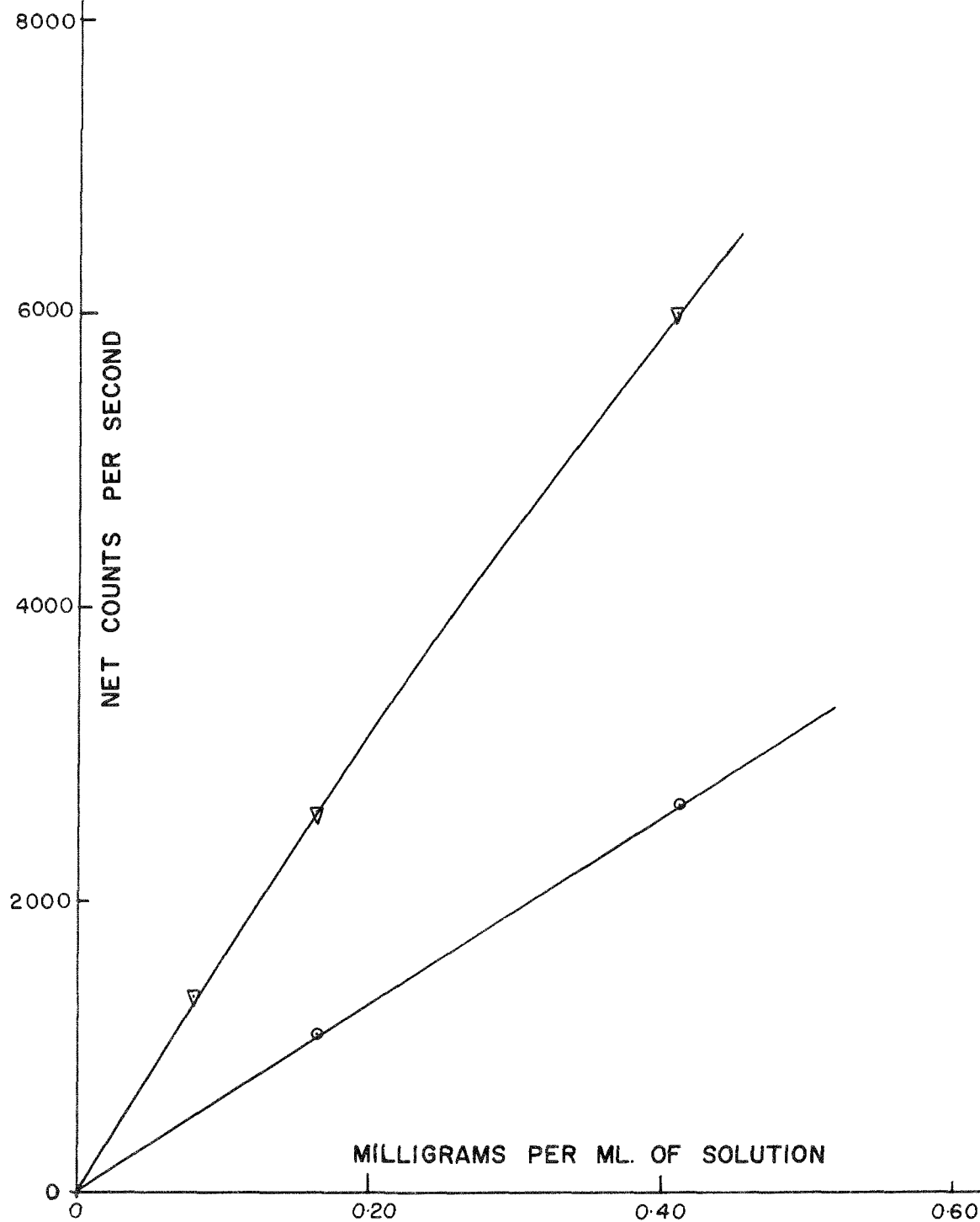


FIGURE 5
DETERMINATION OF URANIUM IN
 UO_2/ThO_2 MIXTURES

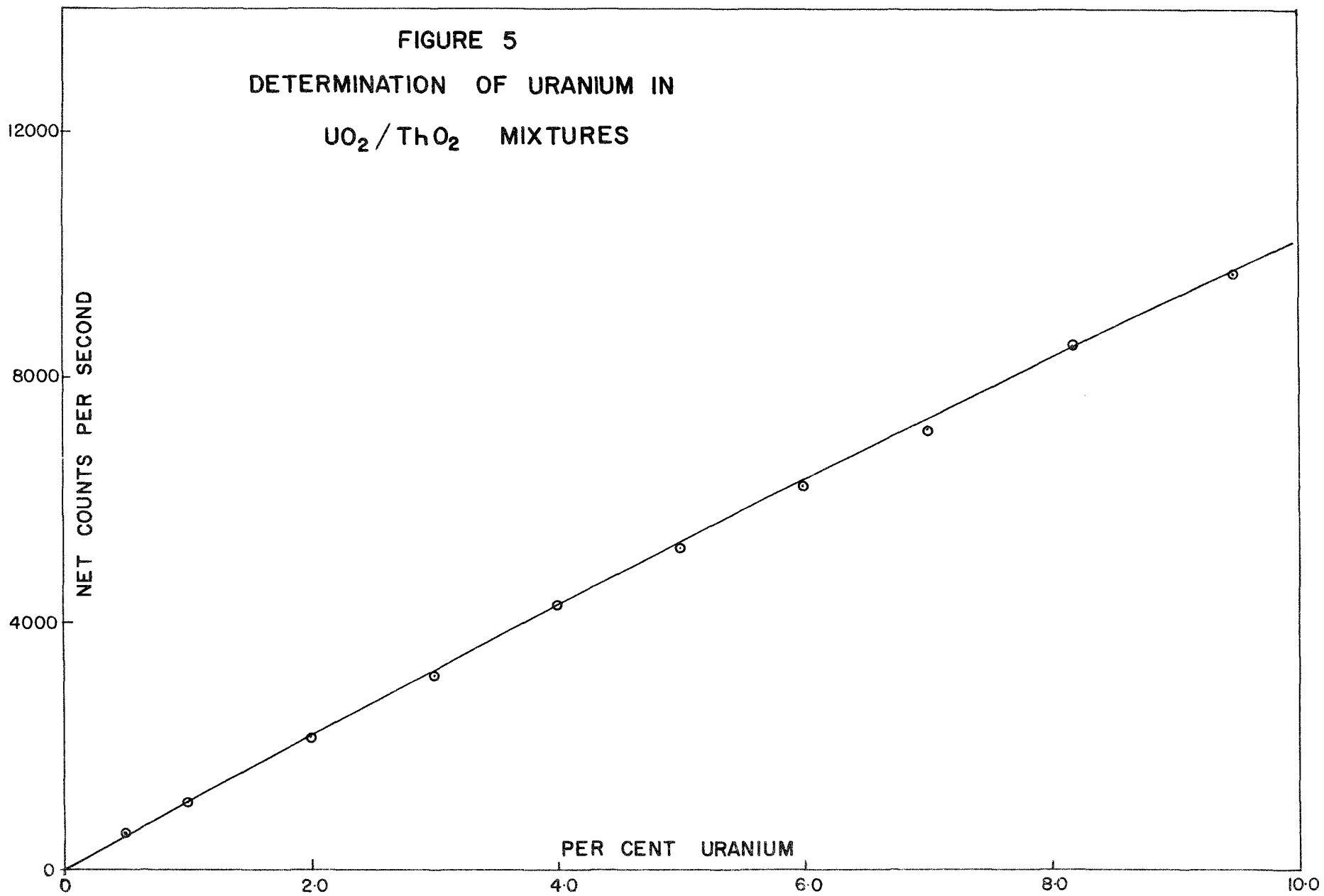


FIGURE 6

DETERMINATION OF THORIUM IN HNO_3 SOLUTION

50 KVP - 50 MA

▽ - Mo TARGET

○ - W TARGET

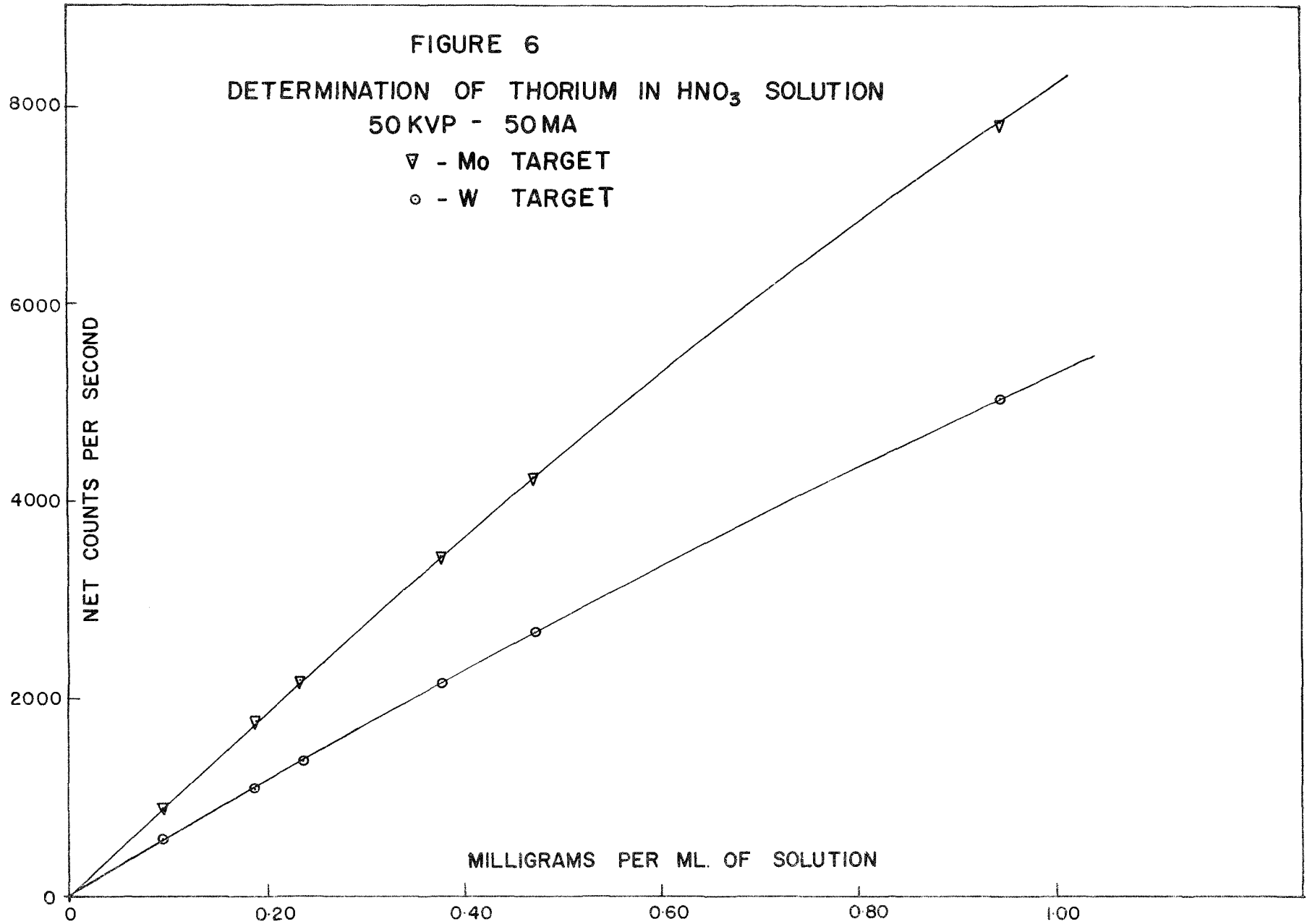


FIGURE 7
DETERMINATION OF THORIUM IN HNO₃ SOLUTION
40 KVP - 40 MA
▽ - Mo TARGET
○ - W TARGET

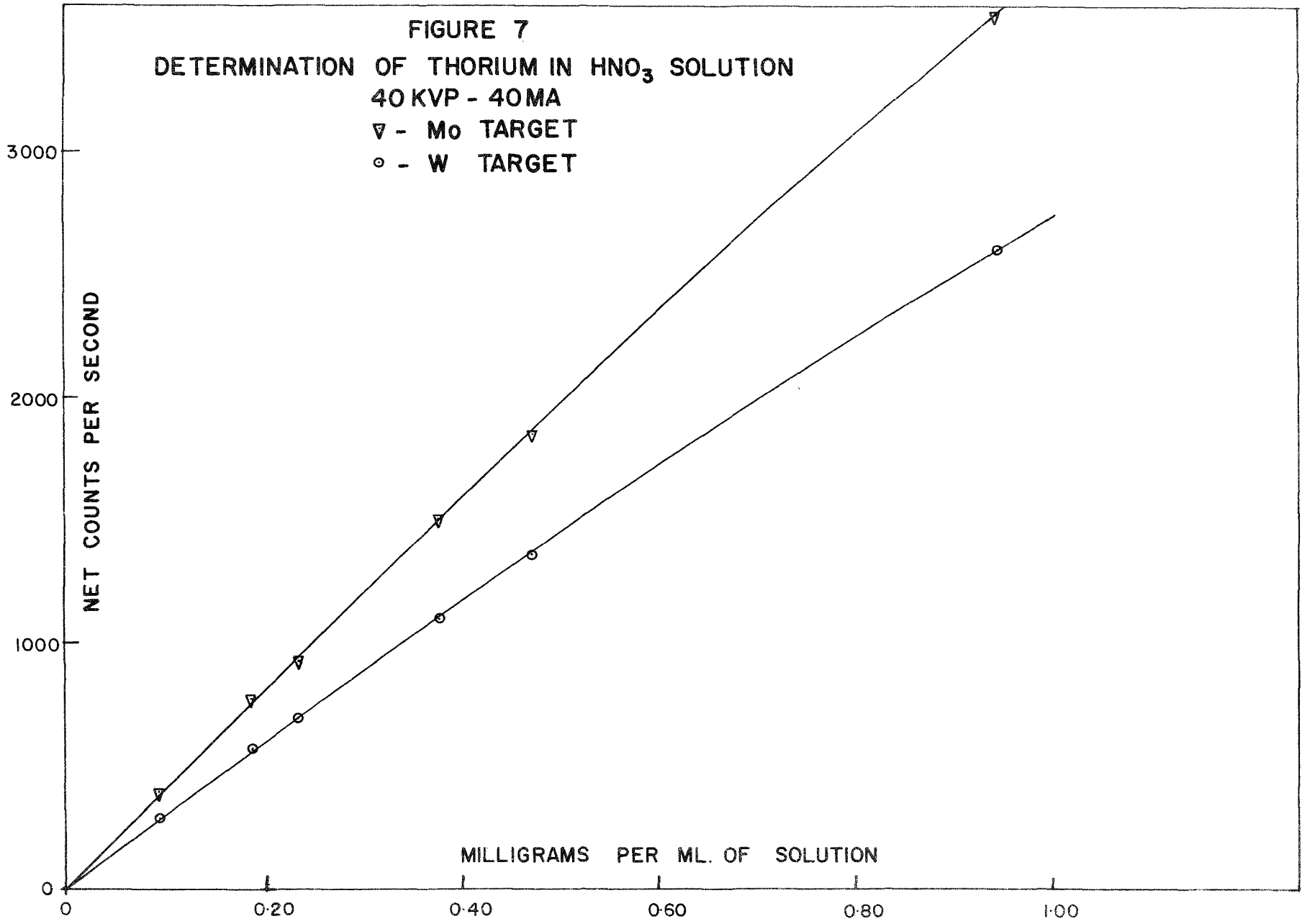
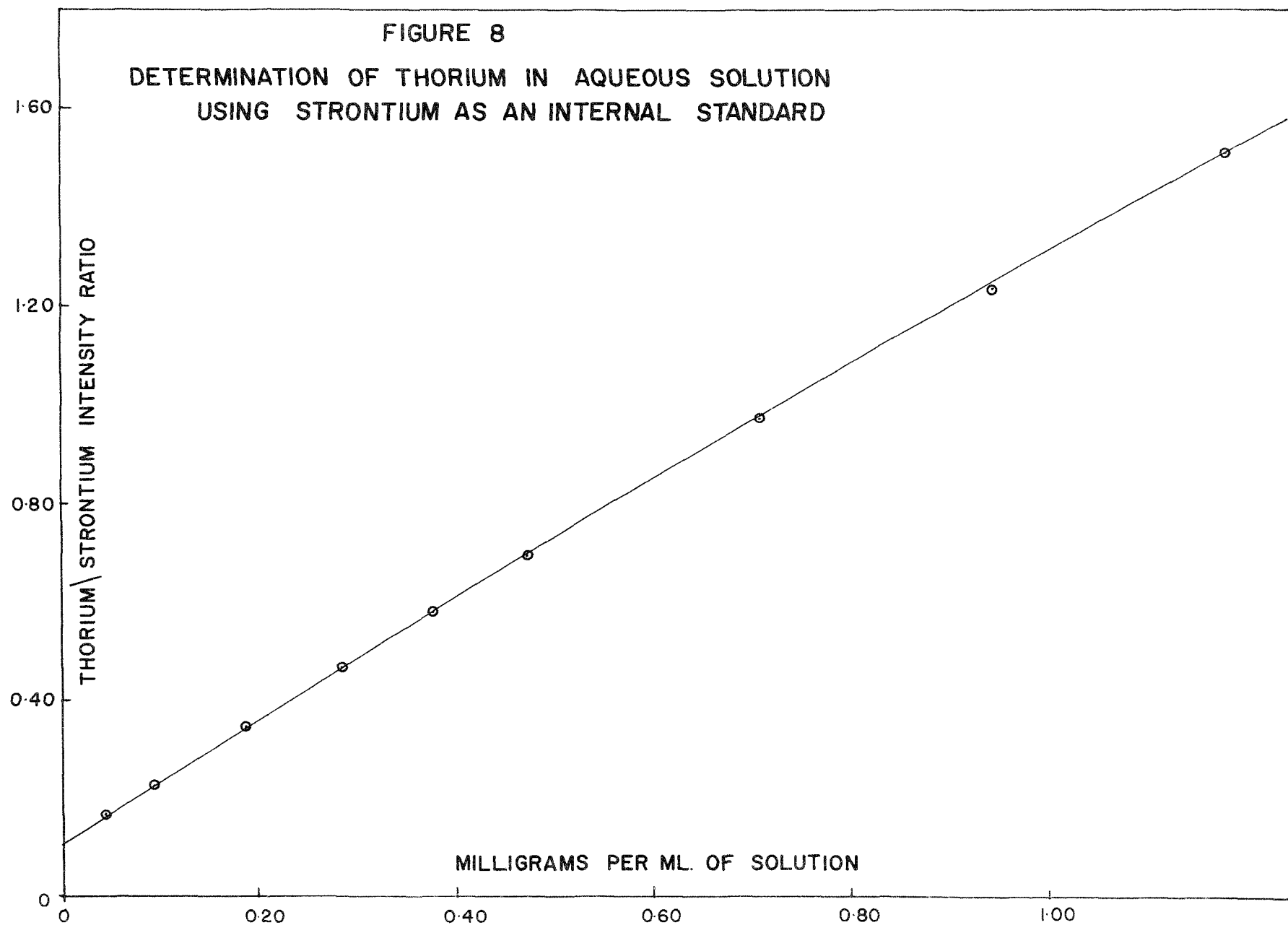


FIGURE 8

DETERMINATION OF THORIUM IN AQUEOUS SOLUTION
USING STRONTIUM AS AN INTERNAL STANDARD



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