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CANADA

DEPARTMENT OF MINES AND TECHNICAL SURVEYS
MINES BRANCH

**MEASUREMENT OF THORIUM IN ORES
BY THE THORIUM EMANATION METHOD**

by

J. B. Zimmerman and J. A. F. Bouvier
RADIOACTIVITY DIVISION

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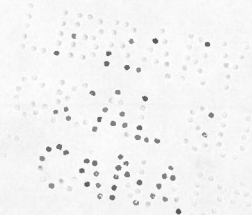
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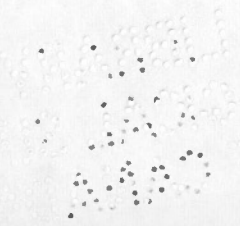
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ABSTRACT

A flow counter for determining the thorium content of ores in secular equilibrium is described.

Scintillations produced in a zinc sulphide phosphor by alpha particles resulting from the disintegration of thoron are detected by a photomultiplier tube and registered by a standard scaling unit.

The counter response is linear and good sensitivity is obtained. The limit of detection is approximately 0.01% ThO₂.

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THE MEASUREMENT OF THORIUM IN ORES BY THE
THORIUM EMANATION METHOD

by

J.B. Zimmerman and J.A.F. Bouvier

INTRODUCTION

Thorium very frequently occurs with uranium in natural ore deposits and although, at the present time, it is not in particular demand for atomic energy purposes, it does attain significance in the metallurgy of uranium as an undesirable impurity.

The frequency with which thorium-containing uranium ores are encountered has increased in the last few years. Analytical laboratories are therefore constantly searching for faster and more reliable thorium-assay methods.

There are several reliable chemical means for the determination of thorium, notable among these being the cellulose-column method of Williams (1). However, most of the chemical methods are quite involved and require the attention of a highly skilled technician.

The thorium-emanation method presented here offers the advantages of simplicity of operation plus high sensitivity and is based on the principle of alpha particle detection that has been used successfully by the authors and others for the determination of thorium in ores (2) and by Senftle and Keevil in geological age determinations (3).

APPARATUS

The apparatus used for the determination of thorium by the emanation method, although differing radically in design from that described by Evans (4) is the same in principle.

A zinc sulphide phosphor and Dumont type 6292 photomultiplier tube combination (Fig. 1a and 1b) is used for alpha detection. The scintillation chamber is composed of a series of concentric Lucite cylinders 2" long 1/8" thick and 2", 1 1/2" and 1" in diameter, the centre being occupied by a 1/2" x 2" Lucite rod. All surfaces of the Lucite pieces except the outside surface of the 2" cylinder are coated with silver-activated zinc sulphide powder.

The zinc sulphide coating (New Jersey Zinc Co., zinc sulphide No. 2330) is applied by first painting the Lucite surfaces with a thin mixture of Glyptal cement and acetone, then dusting the zinc sulphide on the coated surface through a piece of clean cloth.

The coated cylinders are mounted on a Lucite manifold 5/8" thick and 2 1/2" in diameter in such a manner that gas flowing through three rows of small perforations in the top of the manifold, rises between the walls of the concentric coated cylinders (detail Fig. 1b). This arrangement has the advantages of (a) good geometry, as the chance of an alpha particle striking the phosphor is high because of the small distance between adjacent cylinder walls, (b) the close proximity of the cylinders walls lessens the effect of turbulence within the rising gas, (c) a large area of phosphor is exposed to possible alpha radiation, and (d) as all the walls are covered by phosphor material there is no loss of scintillations due to the absorbance of thoron on the scintillator walls.

The phosphor assembly is attached to a Dumont 6292 photomultiplier tube by means of a Lucite yoke such that a small space is left between the phosphor and the window of the tube for the free escape of the partially spent activating gas. The Lucite yoke comprises two Lucite rings with a piece of soft rubber between (Fig. 1a). Tightening the bolts of the yoke squeezes the rubber slightly from between the rings, holding the yoke firmly on the photomultiplier tube.

The voltage-dividing chain for the photomultiplier tube is contained in a cylindrical Lucite container firmly attached to the base of the tube socket. Inserted through the top of the Lucite cylinder is a removable container designed to expose a drying agent such as silica gel to the voltage-dividing network.

The thorium sample in acid solution is placed in a cylindrical, glass, sample holder (Fig. 2) closed at the bottom and top with rubber stoppers. A fritted-glass filter tube passes through the bottom stopper and allows air under pressure to be diffused through the sample in small bubbles. The top stopper has a piece of glass tubing passing through it which allows the thoron enriched gas or air to pass first through a water-cooled condenser, then to the alpha detecting combination (Fig. 2).

The sample holder is easily filled or emptied of sample solution, and rinsed clean, by disengaging it from the supporting clips and removing one or both stoppers.

A slight flow of air is required when filling the sample holder to prevent a portion of the sample solution from backing up through the fritted-glass diffuser.

Air for entraining the thoron is fed to the sample holder from a gasometer constructed from two 13-gallon polyethylene carboys as shown in Fig. 3. This arrangement gives a head of pressure which is sufficiently constant for a thorium determination.

The bottom carboy is filled with water; then air from a compressed air line or portable pump is forced into it, raising the water through the

siphon to the top carboy. When nearly all the water is raised, with sufficient left to cover the bottom end of the siphon, the air is turned off. Opening a valve on the top of the bottom carboy allows air under pressure from the head of water in the siphon to flow first through a modified Venturi flow-meter (5) then through the sample solution.

One filling of the top carboy is sufficient to run the apparatus for one day.

The scintillations from the phosphor are amplified by the photomultiplier tube and fed to a scaler, such as Nuclear Instrument Co. Model 182 A.

An outline of the apparatus is shown in Fig. 4. Fig. 5 is a photograph of the present apparatus, and Fig. 6 is a photograph of the phosphor-photomultiplier combination for alpha detection.

DETERMINATION OF OPERATING CONDITIONS AND CALIBRATION

After the apparatus has been set up (Fig. 4), and a trial run made with a standard thorium solution, it is ready to be tested to determine the optimum working conditions.

It is quite apparent that the short half-life of thoron (54.5 seconds) makes it impossible to take a lengthy observation on a stationary volume of gas. The gas sample must, therefore, be fed continuously in a steady stream to the scintillator from the sample where it is being produced continuously by the disintegration of thorium X, a decay product of thorium. The rate at which the steady stream of gas arrives at the scintillator is important. A rate which is too slow would allow most of the thoron atoms to decay before reaching the scintillator and too fast a rate would cause most of the thoron atoms to pass through the scintillator before disintegration. Optimum flow rate can be determined mathematically (4) from the parameters of the flow system by using the formula:

$$F \text{ max} = \frac{\lambda V_1}{\log_e \left(1 + \frac{V_1}{V_2}\right)}$$

where λ is the decay constant for thoron, V_1 is the volume of the scintillator chamber, and V_2 the volume of the system from the surface of the solution in the sample holder to the scintillator.

A more practical way to determine the maximum flow is to draw a flow curve (Fig. 7) by varying the rate of flow of air through the sample and plotting the count rate registered by the scaling unit vs. flow-meter reading. The flow curves have a characteristic broad top which allows considerable variation on each side of the optimum flow-rate.

The detecting system can be operated at its greatest sensitivity by increasing the voltage applied to the photomultiplier tube. However, there is a limit to which the voltage can be raised and still distinguish counts due to thoron, as the noise level of photomultiplier tubes increases with increased voltage, thus raising the background count.

If a plot of S^2/b vs. V is drawn (where "S" = corrected counts/minute due to the sample, "b" = counts/minute due to background, and "V" = voltage applied to the photomultiplier tube there is a point where the ratio begins to decrease with increasing voltage (Fig. 8)*. The voltage at this point produces optimum sensitivity for the particular photomultiplier tube used in the instrument when the scaling-unit controls are kept at a constant setting.

After optimum operating conditions have been established, calibration is carried out by running different amounts of a thorium standard and drawing a graph of net counts/minute due to sample vs. thorium content in milligrams ThO_2 . A typical curve is shown in Fig. 9. In practice a standard sample is run each day to check the calibration. A continuous run of samples and standards will produce a gradual increase in the background counting rate. Fig. 10 shows such an increase due to 19.2 mg. ThO_2 . The emanation from this amount contacted the phosphor for 105 minutes out of a total run time of 300 minutes.

The background count above that due to natural disintegrations within the phosphor is due to alpha rays produced in the disintegration of thorium C^1 and C^{11} , daughter products of thoron which have very short half-lives of 0.3 micro-seconds and 3.1 minutes respectively. These two alpha-emitting elements quickly reach equilibrium with the longest-lived member left after the disintegration of thoron, and decay with the half-life of thorium B, i.e. approximately 10.6 hours. This is shown in Fig. 11 which is a plot of the background decay from a highly contaminated phosphor.

In practice, the increase in background counts is very small compared to the number of sample counts taken.

The total number of counts contributing to a sample count are derived from alpha particles produced in the disintegration of thoron, half-life 54.5 seconds; thorium A, half-life 0.16 seconds; thorium C^1 , half-life 0.3 micro-seconds; thorium C^{11} , half-life 3.1 minutes; and natural disintegrations within the phosphor and walls of the scintillator.

* Measurements taken were insufficient to determine exactly the character of the apex of Fig. 6. However the ratio was changing rapidly and the top of the curve would be narrow.

Thoron and thorium A contribute upwards of 98 per cent of the total scintillations due to the presence of thorium in a sample (4). Therefore, if a background count is taken before and after a sample count and the average deducted from the sample count, a straight-line relationship exists between sample net count rate and thorium concentration.

Uranium is very often associated with thorium in ores but due to the long 3.82-day half-life of radon (the gaseous member of the uranium family) compared to thoron, very little of it decays in the time it takes the thoron-enriched gas to pass through the scintillator at the optimum flow rate. Fig. 12 illustrates graphically the non-interference of uranium on a thorium determination when the ratio of uranium to thorium is as high as one hundred to one.

SAMPLE PREPARATION

Two means of preparing samples for the determination of thorium by the emanation method have been used (4): (a) The sample is taken completely into solution, and (b) the sample is fused and de-emanated while in the molten state. Of the two methods, the complete solution of the sample has proved most satisfactory. The sample aliquot used in the determination should be as dilute as possible in salts, and as free as possible from colloidal suspensions of silica. Large quantities of salts decrease the emanating power of a solution, where emanating power may be considered as the ability of the solution to give up its thoron to the entraining gas. Colloidal silica is particularly detrimental as it has high absorption for thoron (4).

Several methods of taking ore into solution have been used successfully depending on the type of ore under consideration. Sulphuric acid must be avoided because thorium X, the parent of thoron, is an isotope of radium and forms insoluble sulphates. A general method that is satisfactory for all ores is as follows: Weigh a sample containing at least 1.0 mg ThO_2 into a nickel crucible and roast for 4 to 5 minutes at approximately 450°C . Cool the roasted ore and cautiously add 10 to 15 ml of concentrated hydrofluoric acid. Evaporate the mixture to near dryness and repeat the hydrofluoric acid treatment three times. Transfer the residue containing the remaining fluorides to a 600 ml Pyrex beaker, washing the crucible with approximately 50 mls of water. Add 5 ml of concentrated nitric acid and 10 ml of concentrated perchloric acid and fume the mixture to near dryness. If fluorides are still in evidence, repeat the perchloric acid fuming until they are destroyed. Cool the fluoride-free sample, add 20 ml of water and boil. If undecomposed ore is present after the treatment just described, filter off the solution and ignite the filter paper and residue in a porcelain crucible. Add 3 gm of sodium peroxide (less if the residue is small), and fuse over a gas flame. Dissolve the melt with water and nitric acid and combine with the filtrate. Boil the combined solutions to drive off any accumulated radon and perform the thorium determination soon after cooling.

Other methods of taking refractory samples into solution that show promise of usefulness are boric-acid fusions in platinum dishes after the hydrofluoric-acid treatment, and sodium peroxide-sugar charcoal fusions of the ore using the Parr bomb (6).

Nitric acid is used as a routine procedure in the final makeup of samples with no deleterious effects on the ZnS phosphor. However, the possibility of using perchloric acid, which is non-volatile at room temperatures, is being investigated.

PROCEDURE AND CALCULATIONS

Standardizing the apparatus is the first step in preparing for thorium analysis by the emanation method. This is accomplished by making up a standard solution containing an approximately known amount of thorium from an aged thorium nitrate compound which is in equilibrium. A portion of this solution is then analysed gravimetrically to determine the exact ThO_2 content.

The amount of thorium in an ore sample is then calculated by comparing the net counts per minute produced by thoron entrainment from 200 ml of sample solution with the net counts obtained by de-emanating 200 ml of standard solution. The standard solution currently in use has a concentration of 19.2 mg ThO_2 per 200 ml.

Assaying a sample involves five steps: (a) initial background reading, (b) standard reading, (c) second background reading, (d) sample reading, and (e) final background reading. The average of the initial and second background is subtracted from the standard reading and the average of second and final background is subtracted from the test sample. In this manner any increase in background due to the decay product of thoron is proportioned. An estimate of the test sample is then made by comparing the counting rate of the unknown with the counting rate of the standard. The justification in using the method of straight line proportion is substantiated by the linearity of the calibration curve (Fig. 9). The extent of the linear portion of the calibration curve has not been determined but it extends at least from 1 to 100 mg of ThO_2 in 200 ml of solution.

The present instrument has a sensitivity such that 19.2 mg ThO_2 gives rise to 428 alpha counts per minute, which is 22.3 counts per minute per mg ThO_2 . An average background reading for a standard 8-minute run will fall between 10 to 25 counts per minute depending upon how long the instrument has been in operation. If a sample is run when the background is low (approximately 10 counts per minute), and since twice background counts is sufficient for assay, then 1 mg of ThO_2 in 200 ml of solution can be detected. If an original 10-gram sample were taken into solution then the lower limit of assay would be 0.01% ThO_2 .

The standard deviation (σ) was calculated on ten standard runs of 19.2 mg ThO_2 per 200 ml of solution, and if expressed as a percentage of the mean, amounts to $\pm 1.73\%$ at the standard concentration level.

Ore samples containing thorium were assayed by several methods and the thorium emanation method was found to be in good agreement with chemical assays. Table 1 shows the comparison of different methods.

TABLE 1

Comparative Assay Results

Ore Designation	Percent ThO ₂		
	Thorium-emanation Method	Cellulose-column Method	Probable Thorium* Radiometric
RA 10096	0.096	0.099	0.21
RA 8884	0.091	0.10	0.21
RA 10862	0.083	0.075	0.32
RA 10696	0.030	0.020	0.054
Monazite Std. # 2601 0.10% ThO ₂	0.11	0.11	0.10
# 6237 6.48% ThO ₂	6.49	6.28	6.48

* Determined by method of Elchholz, Hilborn and McMahon (7)

CONCLUSION

The thorium emanation method has not had as wide an application for the determination of thorium as it deserves, probably because of its dependence upon the secular equilibrium of thorium and because earlier counting methods were not sufficiently consistent. However, wherever ore samples are assayed for thorium it can be a valuable tool, especially for low concentrations of thorium where purely chemical methods meet with difficulties, and as an independent check on chemical assays in the higher ranges of concentration. Little time is required when the method is used for checking purposes as a portion of the solution used for chemical analysis can be utilized for a thoron determination with the added advantage that none of the sample is destroyed.

An added feature of alpha detection by scintillation rather than by ionization is that air instead of nitrogen may be used for entraining thoron.

The method and apparatus have proved that thorium assays may be performed with precision and accuracy and with much greater speed than purely chemical analysis for thorium ores in equilibrium.

REFERENCES

- (1) Williams, A.F. Analyst, 77 279-306 (1952)
- (2) Senftle F.E., Horwood J.L., and Zimmerman J.B., Progress Report 1C-2 Dept. of Mines and Technical Surveys, Mines Branch, Ottawa, Canada (1948)

also

Senftle F.E., Zimmerman J.B., and Dube Y., Mines Branch Report TR-16/49 (1949)

- (3) Senftle F.E. and Keevil, N.B., Trans Amer. Geophys., Union, 28 732-738 (1947)
- (4) Evans, R.D., Rev. Sci.Inst. 6, 99, 1953
- (5) K.H. Todhunter, Journal Sci. Inst. 32, # 1, Jan. (1935)
- (6) Ingles, J.C., Mines Branch Report TR-131 (1955)
- (7) Eichholz G.G., Hilborn N.W., and McMahon C., Can. J. Physics 31, 613-628 (1953)

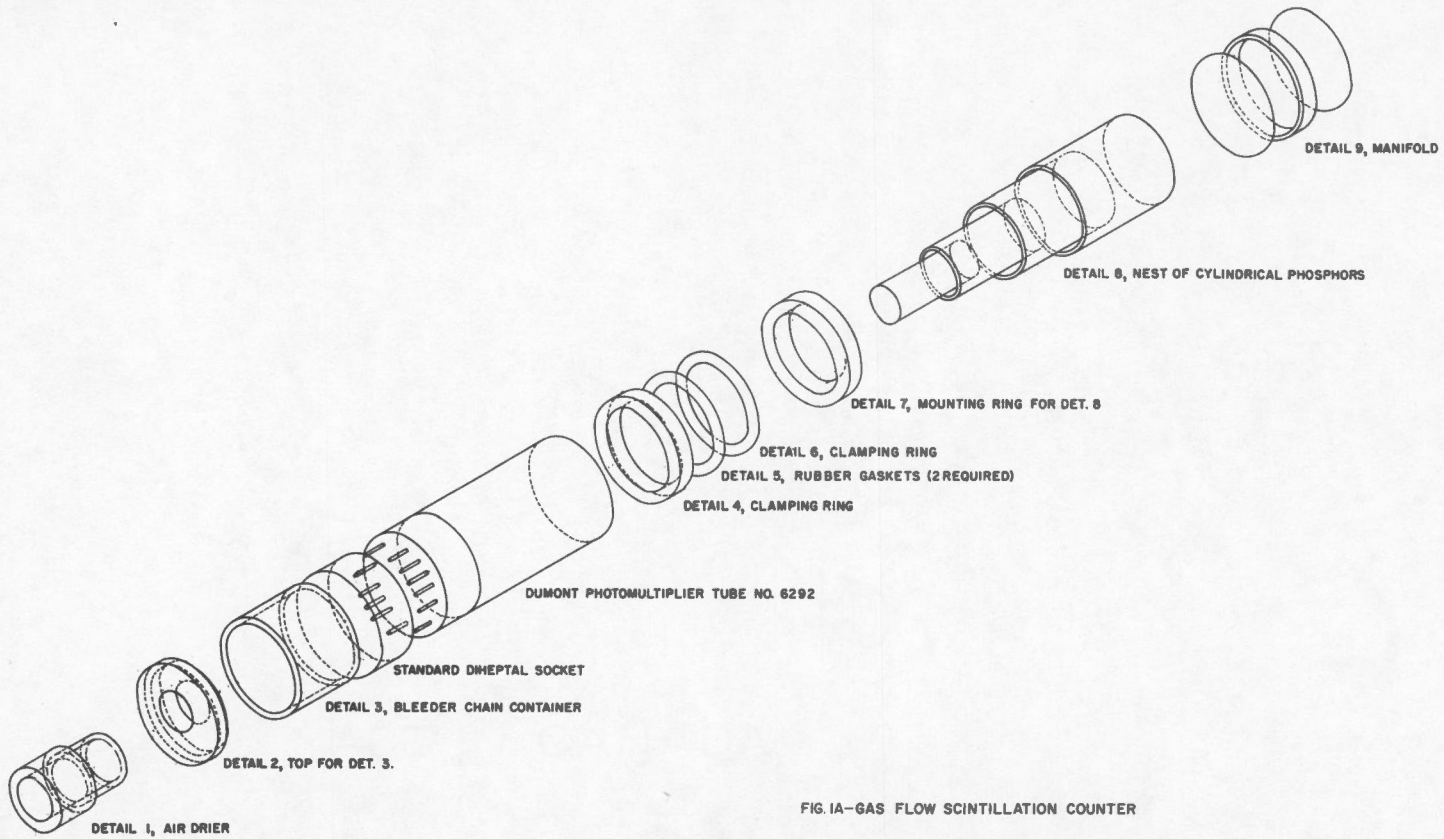
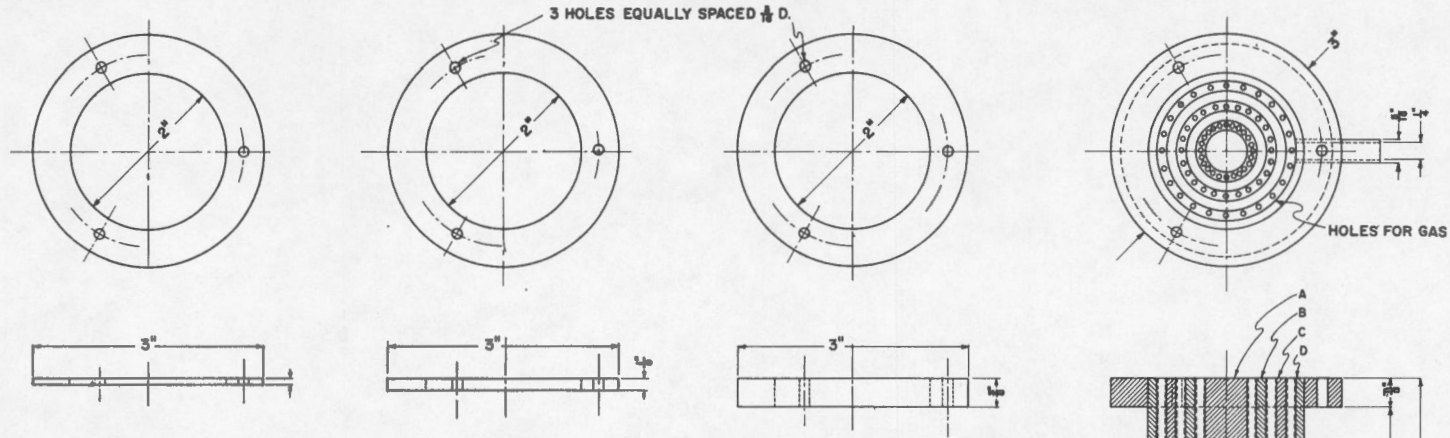


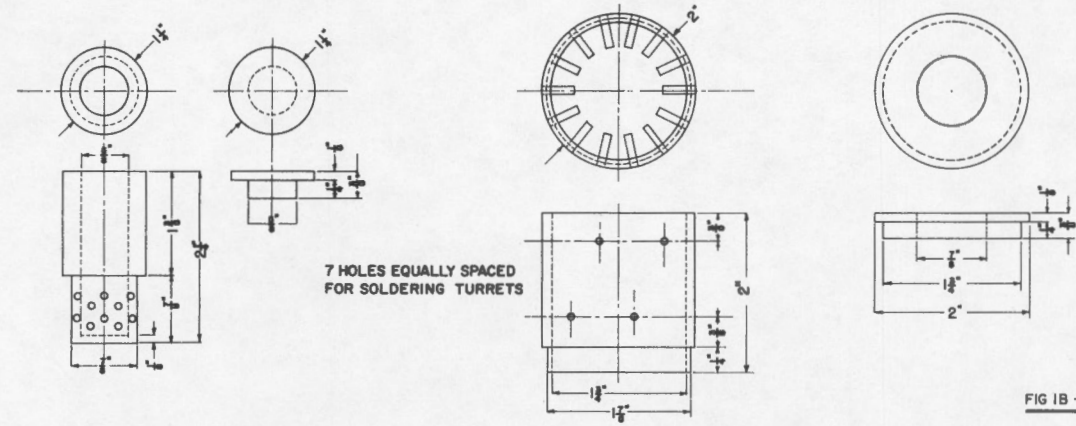
FIG. 1A-GAS FLOW SCINTILLATION COUNTER

C.A. JOBLING



DETAIL 5, GASKETS, RUBBER, 2 REQ'D DETAIL 6, CLAMPING RING, LUCITE, 1 REQ'D DETAIL 4, CLAMPING RING, LUCITE, 1 REQ'D

2" DIAMETER ON DETAILS 4,5,6 SLIP FIT ON PHOTO TUBE



DETAIL 1, AIR DRIER, LUCITE, 1 REQ'D

DETAIL 3, BLEEDER CHAIN CONTAINER, LUCITE, 1 REQ'D

DETAIL 2, TOP FOR DETAIL 3, LUCITE, 1 REQ'D

- A. LUCITE ROD $\frac{1}{4}$ " D. COATED
- B. LUCITE TUBE 1" O.D. $\frac{1}{8}$ " WALLS
- C. LUCITE TUBE $1\frac{1}{2}$ " O.D. $\frac{1}{8}$ " WALLS
- D. LUCITE TUBE 2" O.D. $\frac{1}{8}$ " WALLS
- COATED WITH PHOSPHOR

DETAIL 8 & 9, NEST OF CYLINDRICAL PHOSPHORS & MANIFOLD, LUCITE, 1 REQ'D

FIG 1B — DETAILS OF FLOW SCINTILLATION COUNTER

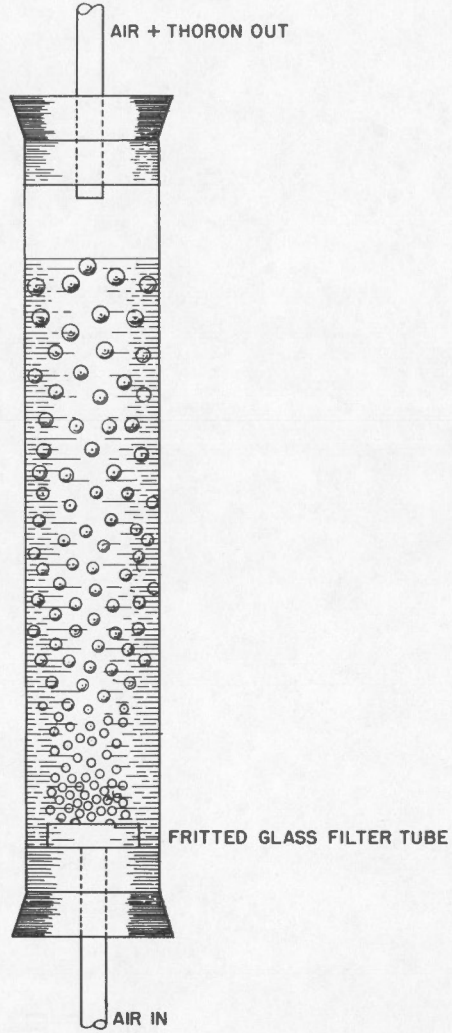


FIG. 2 — SAMPLE HOLDER

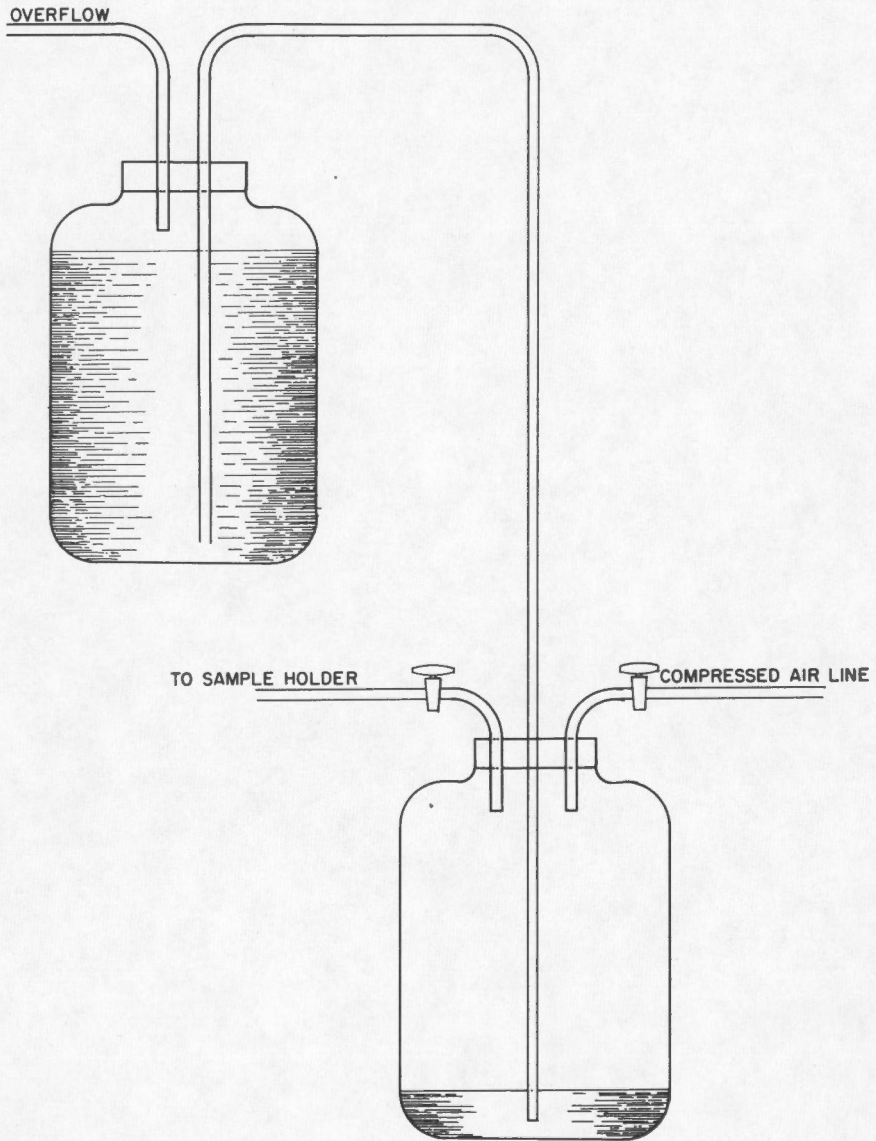


FIG. 3 — GAS PRESSURE SYSTEM

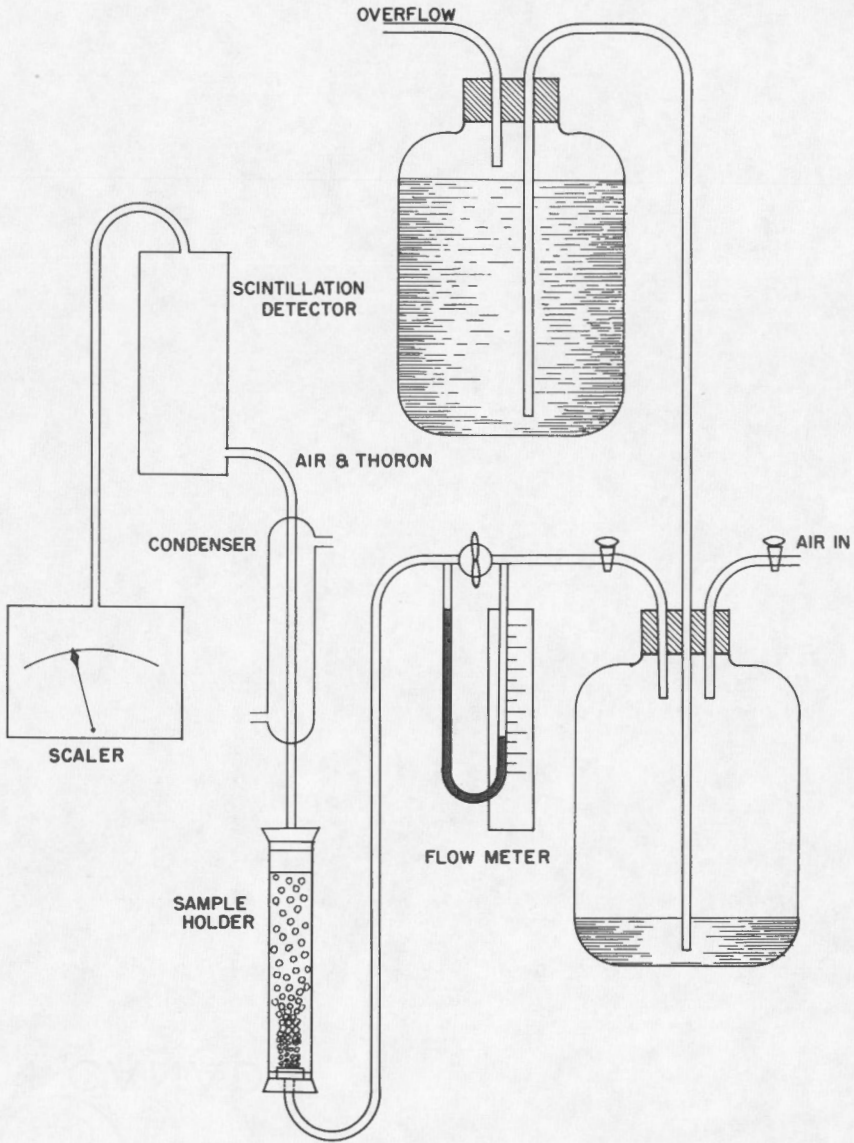


FIG. 4—OUTLINE OF APPARATUS

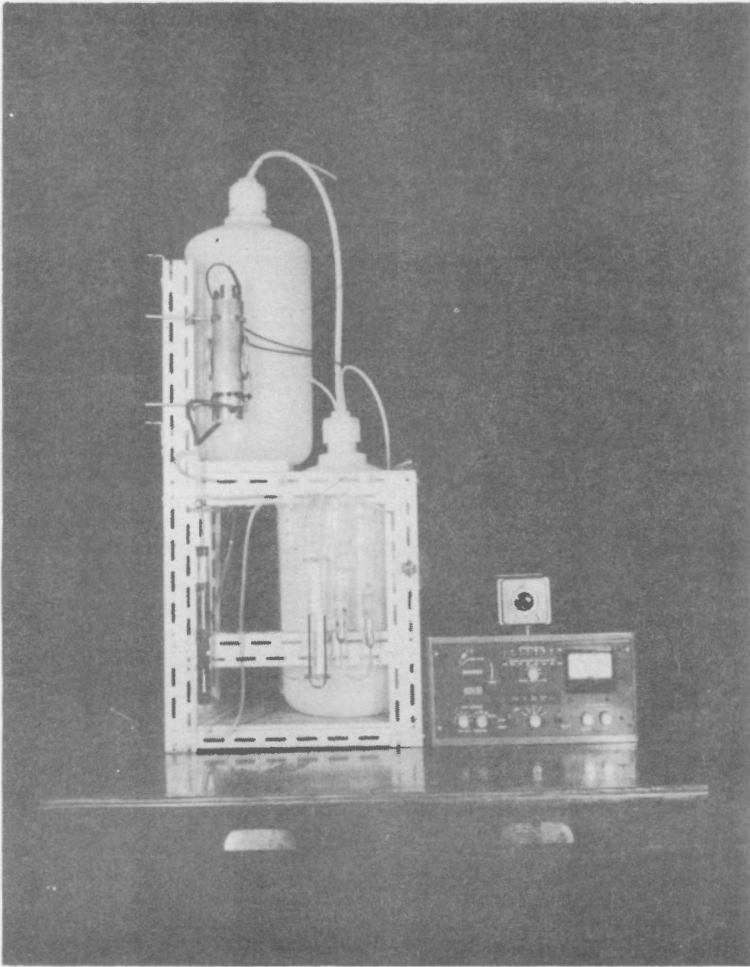


Fig. 5 – Thorium Emanation Apparatus

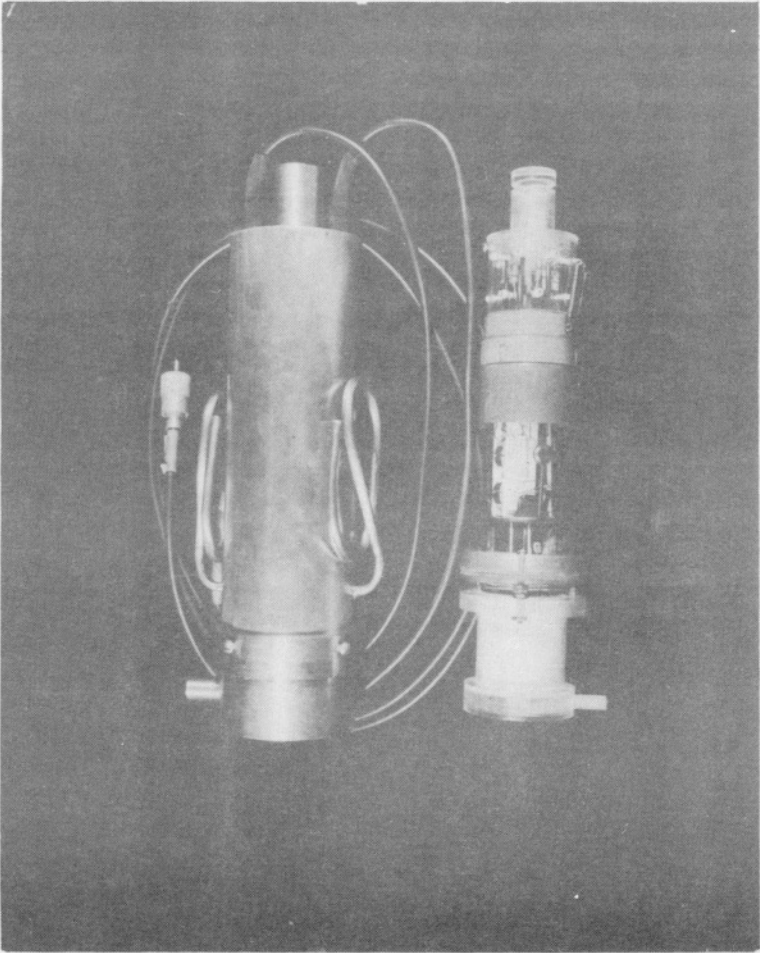


Fig.6 — Phosphor- Photomultiplier Combination.

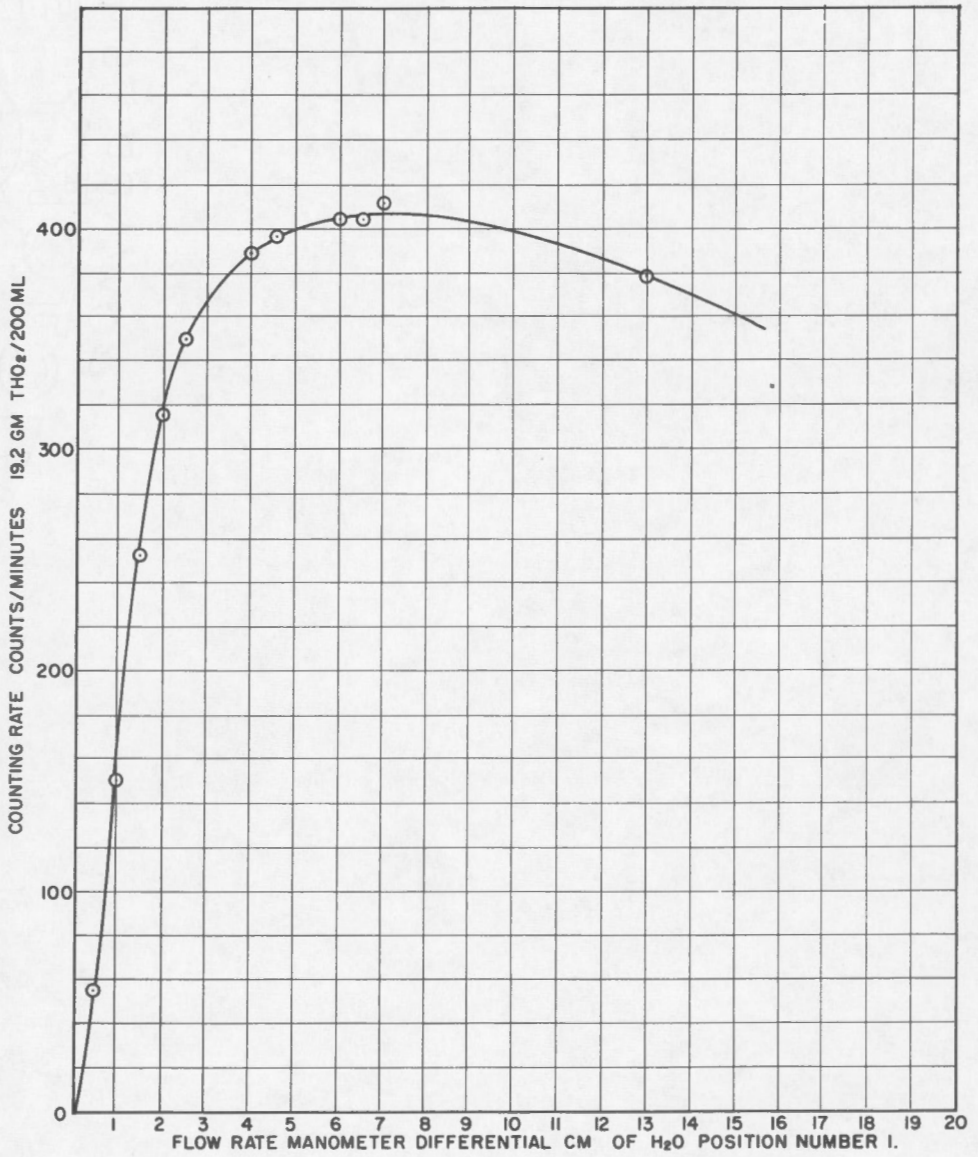


FIG. 7 — THORON FLOW CURVE

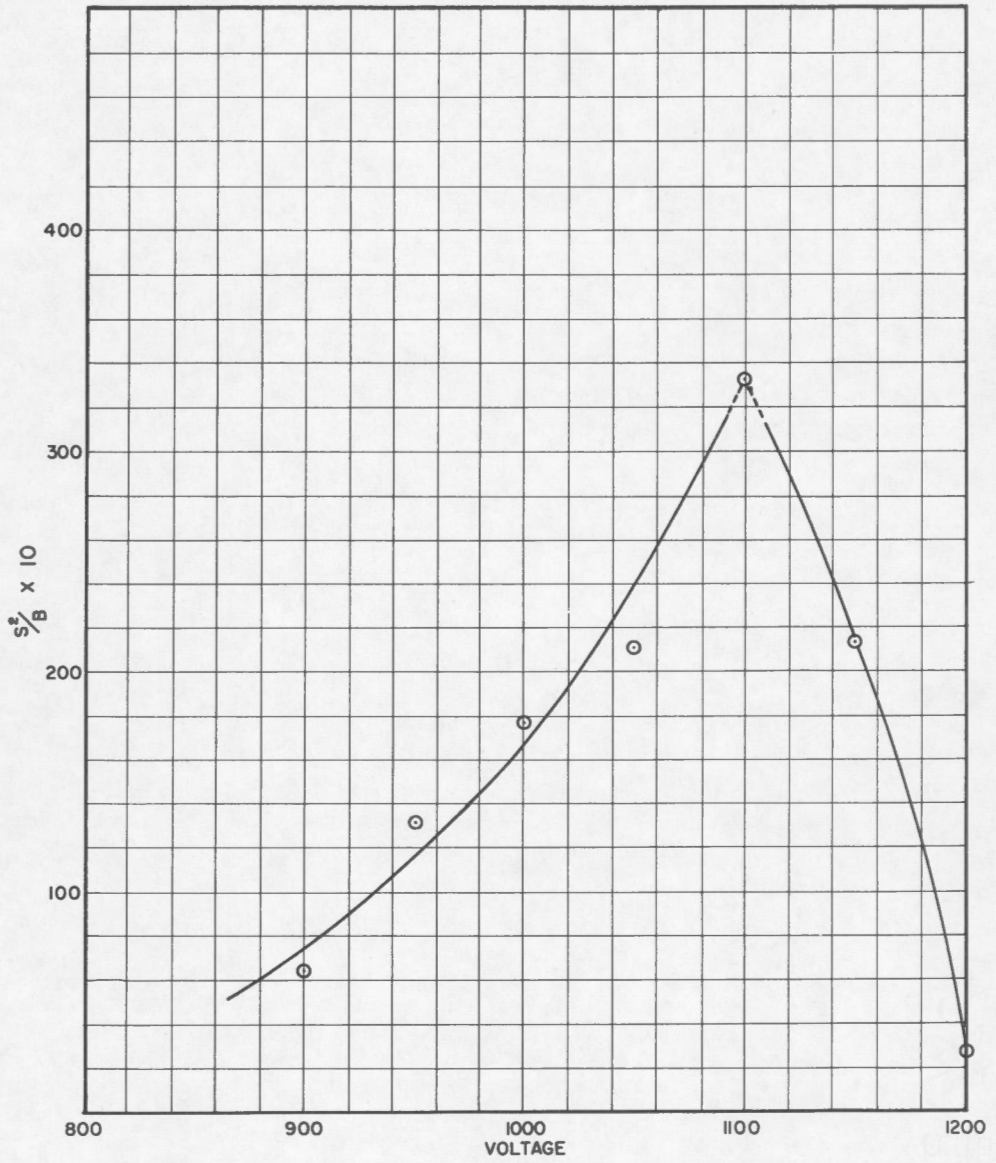


FIGURE 8 - OPTIMUM VOLTAGE SETTING

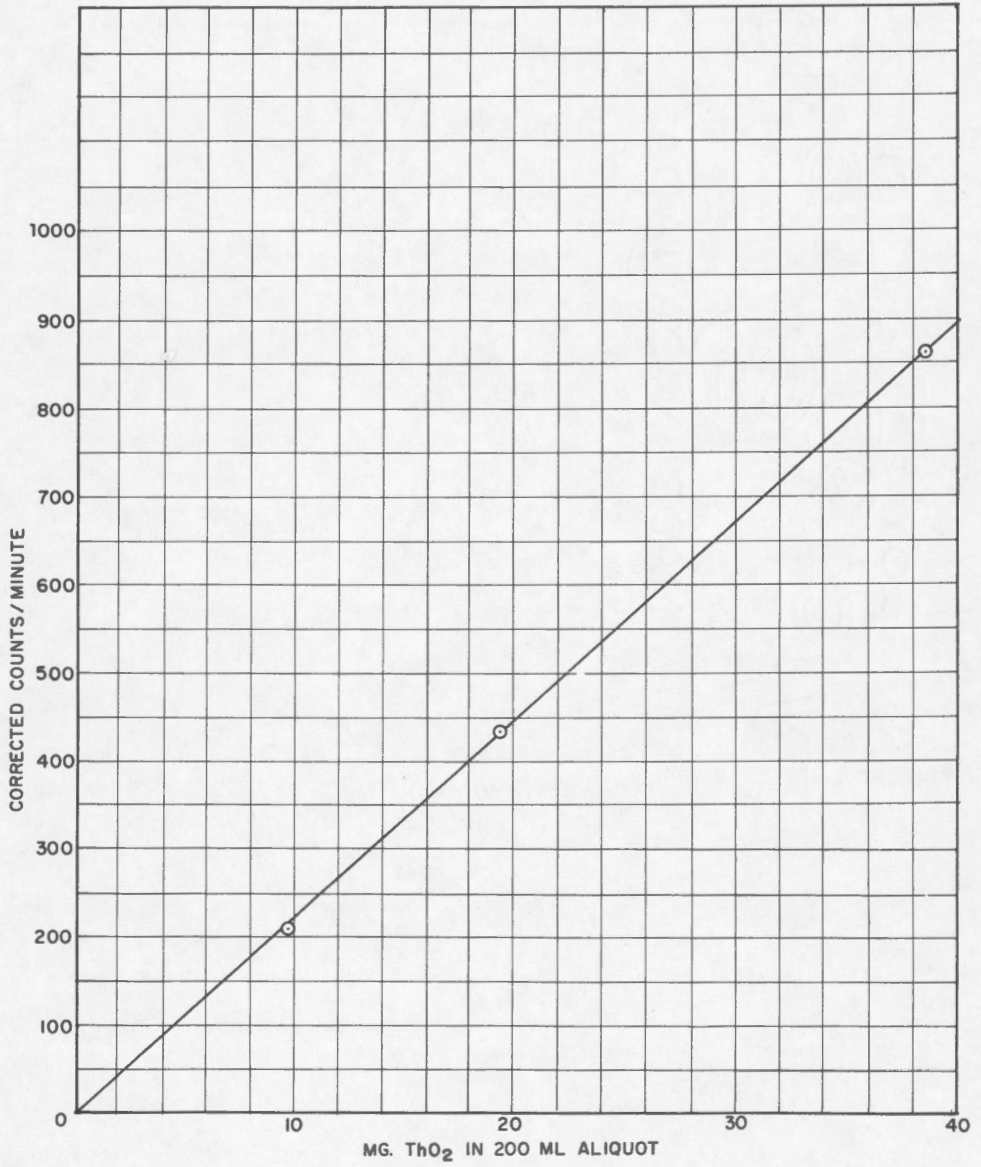


FIG. 9—CALIBRATION CURVE

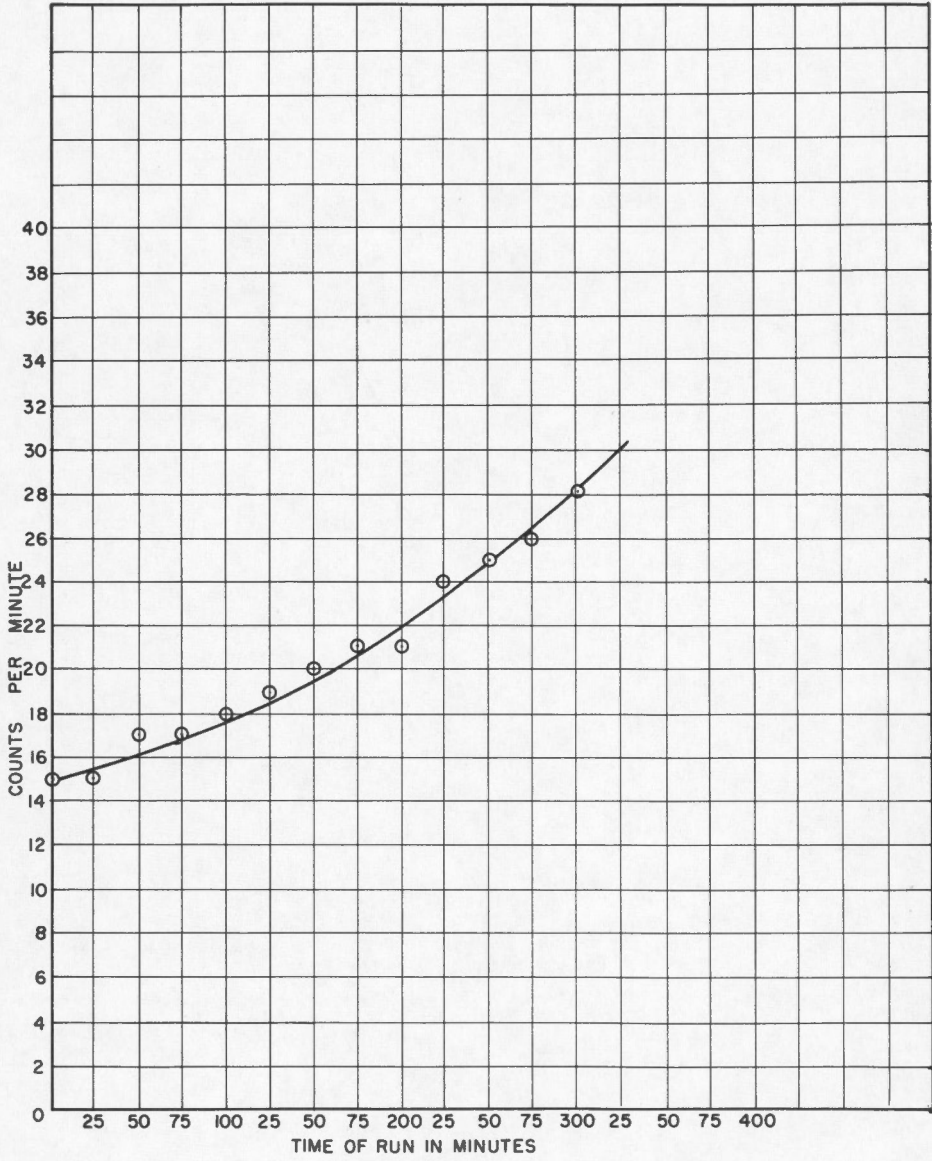


FIG. 10—INCREASE IN BACKGROUND COUNTING RATE

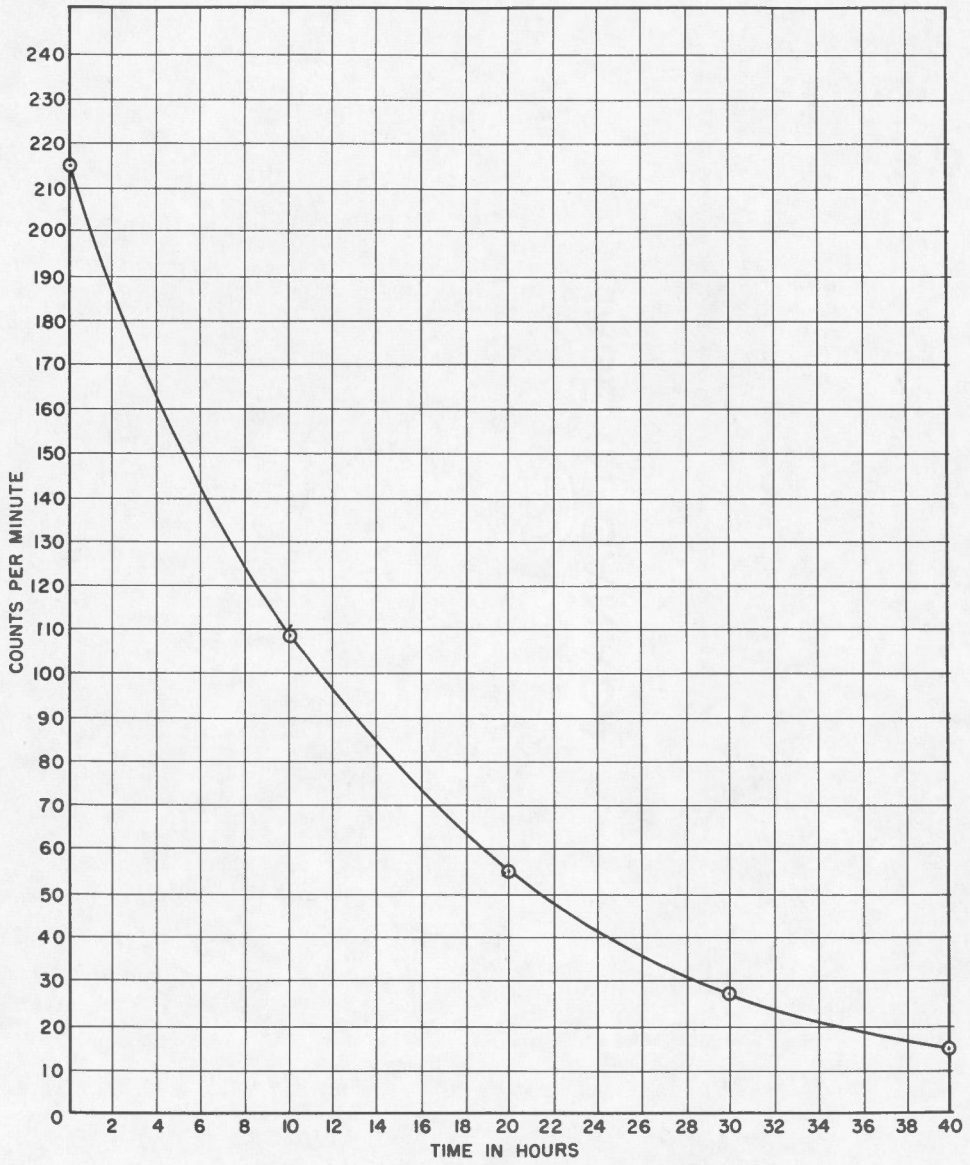
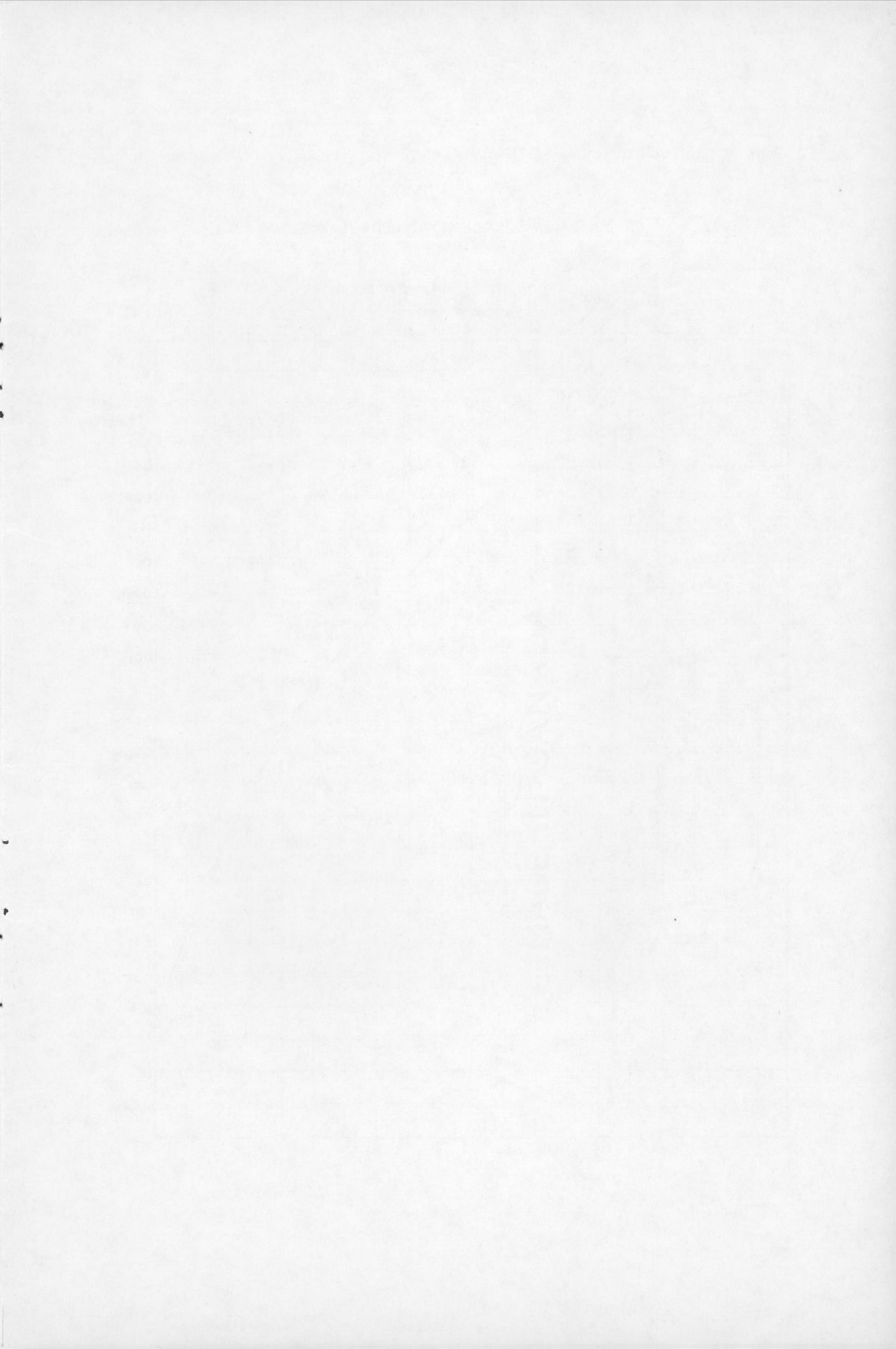


FIG.II — DECAY OF HIGH BACKGROUND WITH HALF LIFE OF ThB



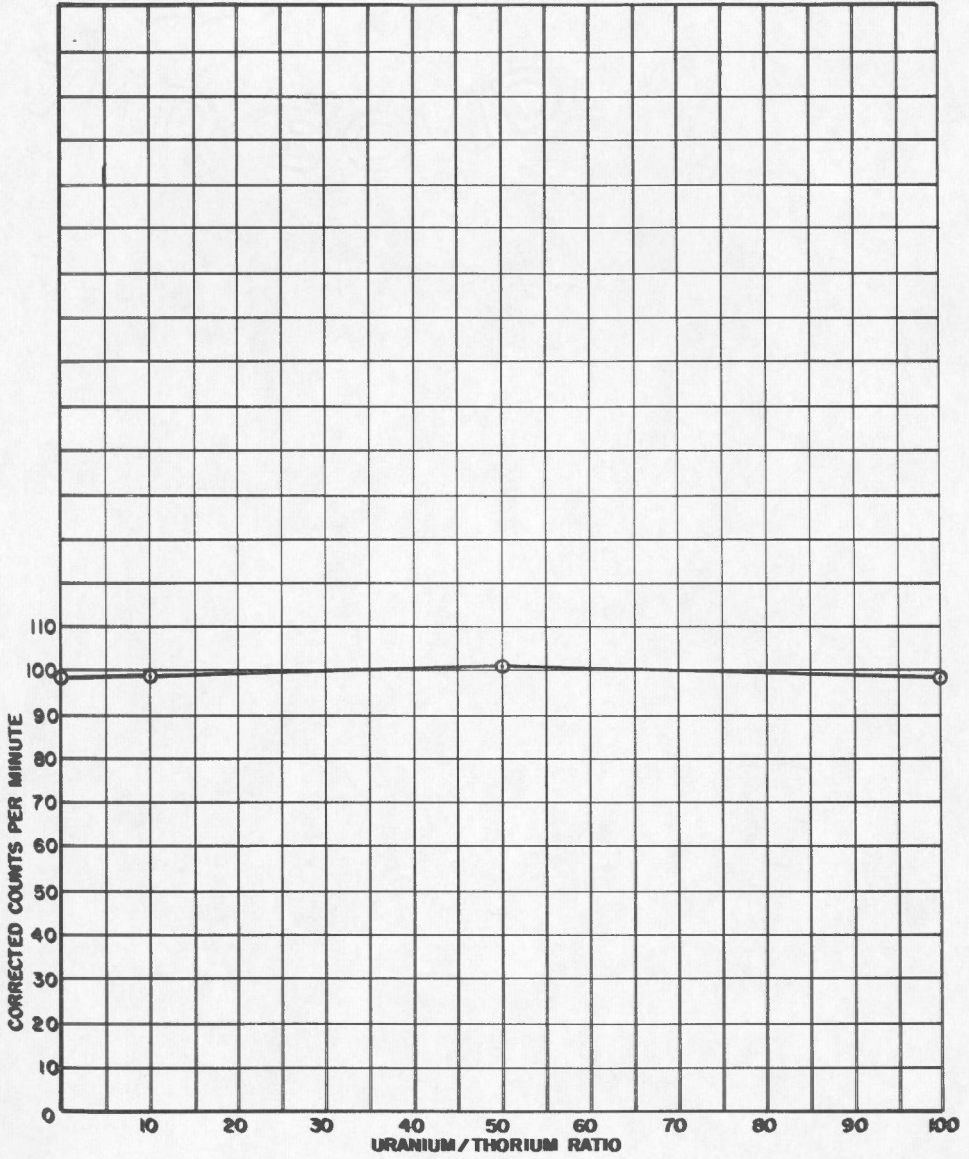
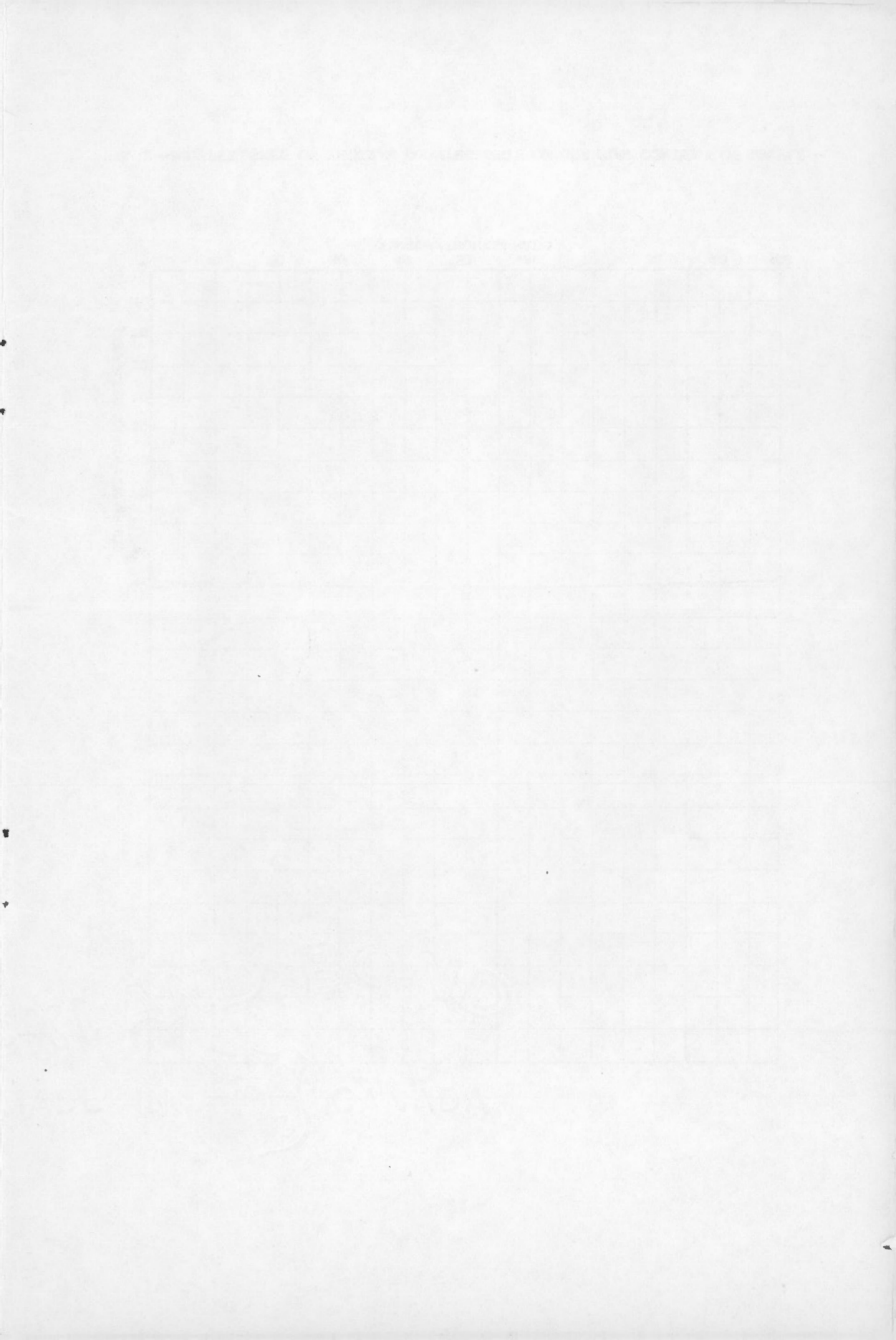


FIG. 12—INDEPENDENCE OF THORIUM COUNTING RATE ON URANIUM CONTENT OF SAMPLE



EDMOND CLOUTIER, C.M.G., O.A., D.S.P.
QUEEN'S PRINTER AND CONTROLLER OF STATIONERY
OTTAWA, 1936