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A GRAPHICAL DETERMINATION OF URANIUM AND THORIUM IN ORES FROM THEIR GAMMA-RAY SPECTRA

by

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MINERAL SCIENCES DIVISION

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A GRAPHICAL DETERMINATION OF URANIUM AND THORIUM IN ORES FROM THEIR GAMMA-RAY SPECTRA

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J.L. Horwood[*]

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SYNOPSIS

A graphical method is described for calculating the uranium and thorium contents of ores. The intersection of straight lines, each relating to a selected interval in the gamma-ray spectrum, makes possible a rapid estimate of the respective contribution of each series (uranium and thorium) to the total gamma activity. The departure from equilibrium in the uranium series and the effect of potassium are both considered. Spectrum curves were plotted for crushed ore samples. Count yields in a number of selected spectral intervals are given for natural uranium, natural thorium, purified uranium oxide (less radium and daughters), and potassium, to illustrate the construction of the linear equations. Typical solutions are shown for several types of ore samples.

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SOLUTION GRAPHIQUE DES SPECTRES DES RAYONS GAMMA ÉMIS PAR DES MINÉRAIS POUR LA DÉTERMINATION DE L' URANIUM ET DU THORIUM

par

J.L. Horwood[*]

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RÉSUMÉ

La présente étude décrit une méthode graphique de calculer la teneur des minerais en uranium et en thorium. L'intersection de lignes droites, dont chacune se rapporte à un intervalle choisi du spectre de rayons gamma, permet de calculer rapidement la contribution respective de chaque série (uranium et thorium) à l'activité totale des rayons gamma. On tient compte du déséquilibre dans la série de l'uranium et de l'influence du potassium. Les courbes spectrales ont été tracées dans le cas d'échantillons de minerai broyé. On donne les relevés numériques dans un certain nombre d'intervalles spectraux choisis dans le cas de l'uranium naturel, du thorium naturel, de l'oxyde d'uranium purifié (moins le radium et les produits de filiation) et du potassium, en vue d'expliquer la construction des équations linéaires. On montre des solutions caractéristiques de plusieurs types d'échantillons de minerai.

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INTRODUCTION

The early radiometric methods of determining the uranium content of ores depended merely upon a measurement of total activity. This was an oversimplification and could lead to serious errors when thorium was present, or when the decay products of uranium, themselves important contributors to the total activity, were not present in their usual proportions (i.e. the uranium ore was "out of equilibrium"). Extreme departures from the equilibrium condition were found in some mill samples as a result of leaching and other chemical processes. However, leaching may also have occurred in nature and led to the formation of secondary minerals. Thus, an excess of uranium relative to the radium daughters could result in some areas, and there might be a deficiency in others.

The development of the "equilibrium method" enabled these problems to be solved if they were encountered separately. This method, based on the solution of simultaneous equations derived from separate beta and gamma determinations, was outlined by Lapointe and Williamson(1), and, independently, by Thommeret(2). Its widespread adoption awaited the development of more sensitive detectors: a counter with adequate sensitivity for this purpose has been described by Eichholz, Hilborn and McMahon(3).

The method is useful for most types of radioactive ore encountered; however, only two sources of activity can be separated from a combination when as many as four independent natural groups of radioactive elements might in fact occur together. As an improvement of that method, operation of the gamma scintillation counter at two or three different gain settings will provide additional information through "energy discrimination". However, with the advent of the scintillation spectrometer it has become more convenient to examine simultaneously a number of separate energy bands, or peaks, in the gamma-ray spectrum(4).

In this way, the separate contributions to the total count from individual emitters, or from groups of emitters, may be found for each of several spectrum regions from standard calibration samples, and may be expressed as the count rate per gram of the oxide within the spectrum region specified, while using a particular sample geometry. In a sample containing a combination of gamma-ray emitters the count rate in a given region, or energy interval, may be expressed as a linear equation

$$C = au + bt + ck + \dots .$$

where a, b, c, ... are constants determined from standard samples. These constants will have various values throughout the spectrum, becoming zero above the highest energy emitted. u, t, k, ... are the weights of the oxides to be calculated.

By a choice of spectrum intervals the equations for the unknowns u, t, k, ... may be solved two at a time, working down the spectrum toward the lower energy levels of radiation.

A number of equations of the form

$$C_1 = a_1u + b_1t$$

$$C_2 = a_2u + b_2t$$

$$C_3 = a_3u + b_3t$$

$$C_4 = \text{etc.}$$

may be conveniently solved using intersecting straight lines in a graphical Cartesian system. From the straight lines (five being a convenient number) which intersect in practice in a small area, the best solution may be found by inspection, rapidly and with an accuracy comparable with the rest of the procedure. The failure of a line to pass through this small area may have some significance, as will be shown later in the examples.

DESCRIPTION OF THE METHOD

In the spectrometer shown in Figure 1, a cylindrical sodium iodide crystal, 5 cm thick by 5 cm in diameter, was mounted on an RCA type 6655 photomultiplier tube as the radiation detector. The pulses from the tube are amplified, shaped, and fed to a multi-channel analyser.[A]

[A] The five-channel Marconi pulse-height analyser (Model CMC 115-935;AEP516) used for most of this work was replaced in later work by a 100-channel transistorized analyser (CDC Model AEP-2230).

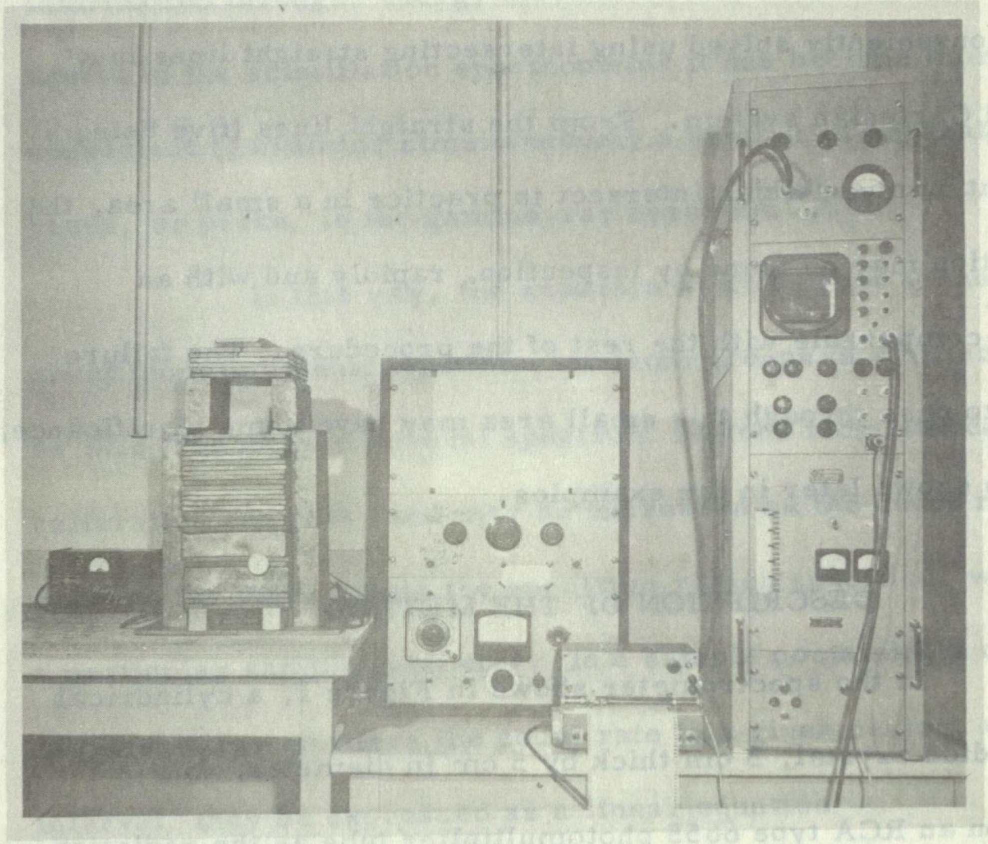


Figure 1. - View of Gamma-ray Spectrometer with CDC 100-channel Analyser

The crystal was mounted with particular attention to factors affecting resolution and the transmission of low-energy gamma rays. The photomultiplier tube was carefully selected for minimum drift with change in count-rate(5). The customary method of calibration was employed, using radioisotopes of known energy levels, such as Co-57, Cs-137, Zn-65 and Co-60. Spectra obtained from natural uranium ore, purified uranium oxide (radium and its daughter elements removed by purification), natural thorium, and potassium are shown in Figure 2.

As is evident from the figure, the gamma-ray spectra of the uranium and thorium series are very complex, with many overlapping peaks. While the thorium series can best be distinguished from the uranium series by measuring the 2.62 MeV gamma-ray from its daughter element Tl 208, so few counts are available from a low-grade sample in this region of the spectrum that additional information must be sought at lower energies where pronounced thorium peaks occur. Uranium and its immediate decay products, in contrast with those following radium, can only be measured with any degree of sensitivity in the low energy region below 0.1 MeV. Potassium, which is weakly radioactive in nature, can be measured by means of its radioactive isotope K-40 using a narrow spectral region around 1.46 MeV, provided that other sources of activity are low. Conversely, because of its low specific activity, potassium is not usually a serious source of error in thorium and

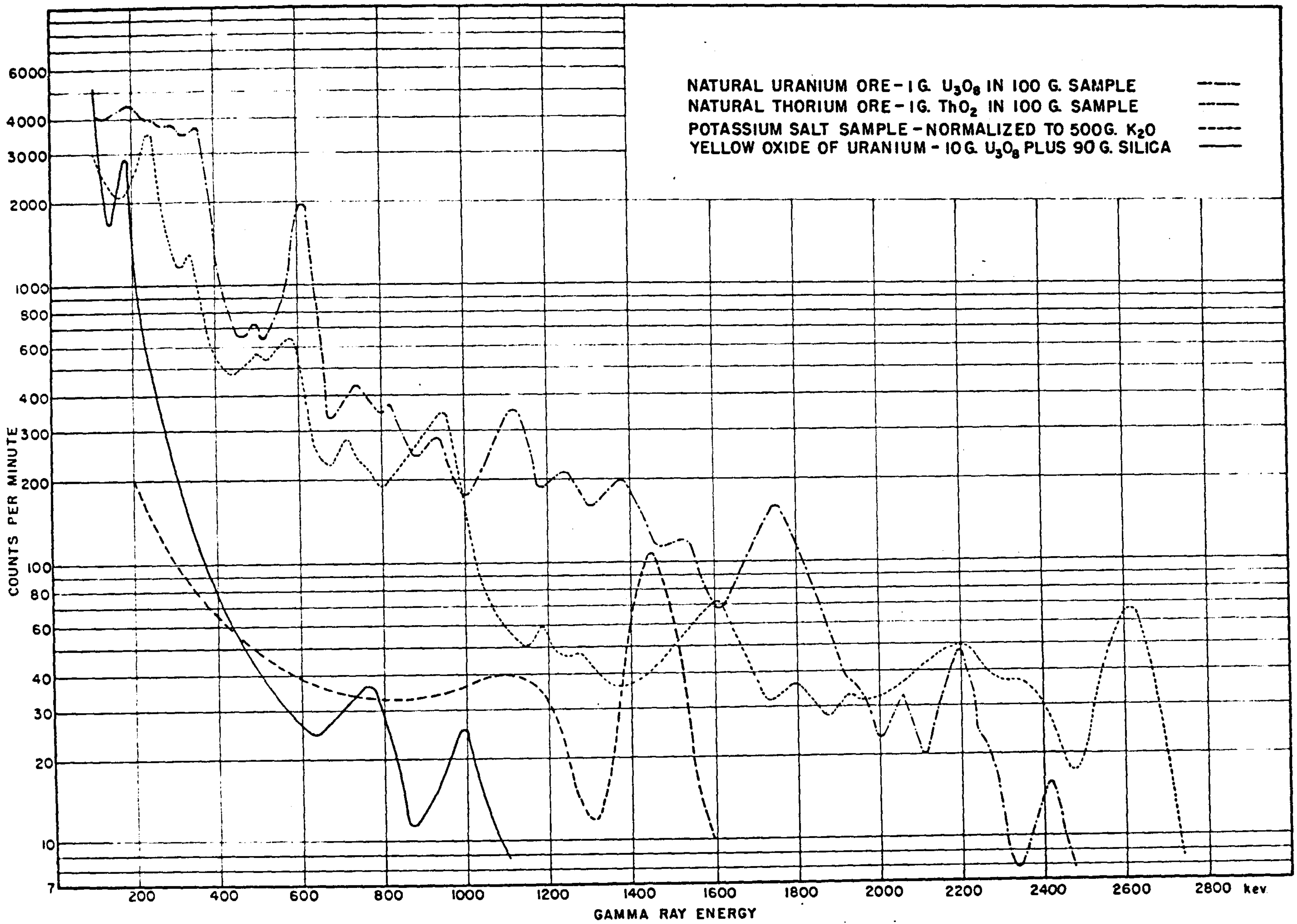


FIG. 2- GAMMA-RAY SPECTRA FROM NATURAL ORES OR THEIR CONSTITUENTS

uranium determinations in other regions of the spectrum. Table 1 shows the count yield at a number of intervals of the gamma-ray spectrum, obtained from standard samples with the particular sample geometry used with this detector. The sample containers were glass jars having an internal diameter of 4.5 cm. Generally, a 100 gram sample was used and the sample thickness was then 5 cm; an empirical correction curve was determined for other sample weights and thicknesses. The curve shows that a very precise determination of sample weight or thickness for a 90 to 110 gram sample is not necessary, since the major contribution to the total count rate originates in the 30 gram fraction closest to the detector; on the other hand, it does indicate the importance of careful sample mixing and the prevention of segregation. This correction curve is not applied below 200 keV, because the effect of self-absorption in the sample becomes increasingly important as the energy decreases.

CALCULATED EXAMPLES

The count yields from the standard samples in Table 1 were combined mathematically to produce a range of imaginary examples to illustrate the use of the graphical method of solution and the required counting time for a given ore grade and composition, ignoring possible effects of drift and statistical fluctuation. These examples are presented in Table 2, and the graphical solutions are shown in Figures 3 to 7. A sample calculation is given in the Appendix.

TABLE 1

Count Yields in Selected Spectral Intervals from Natural Emitter Groups

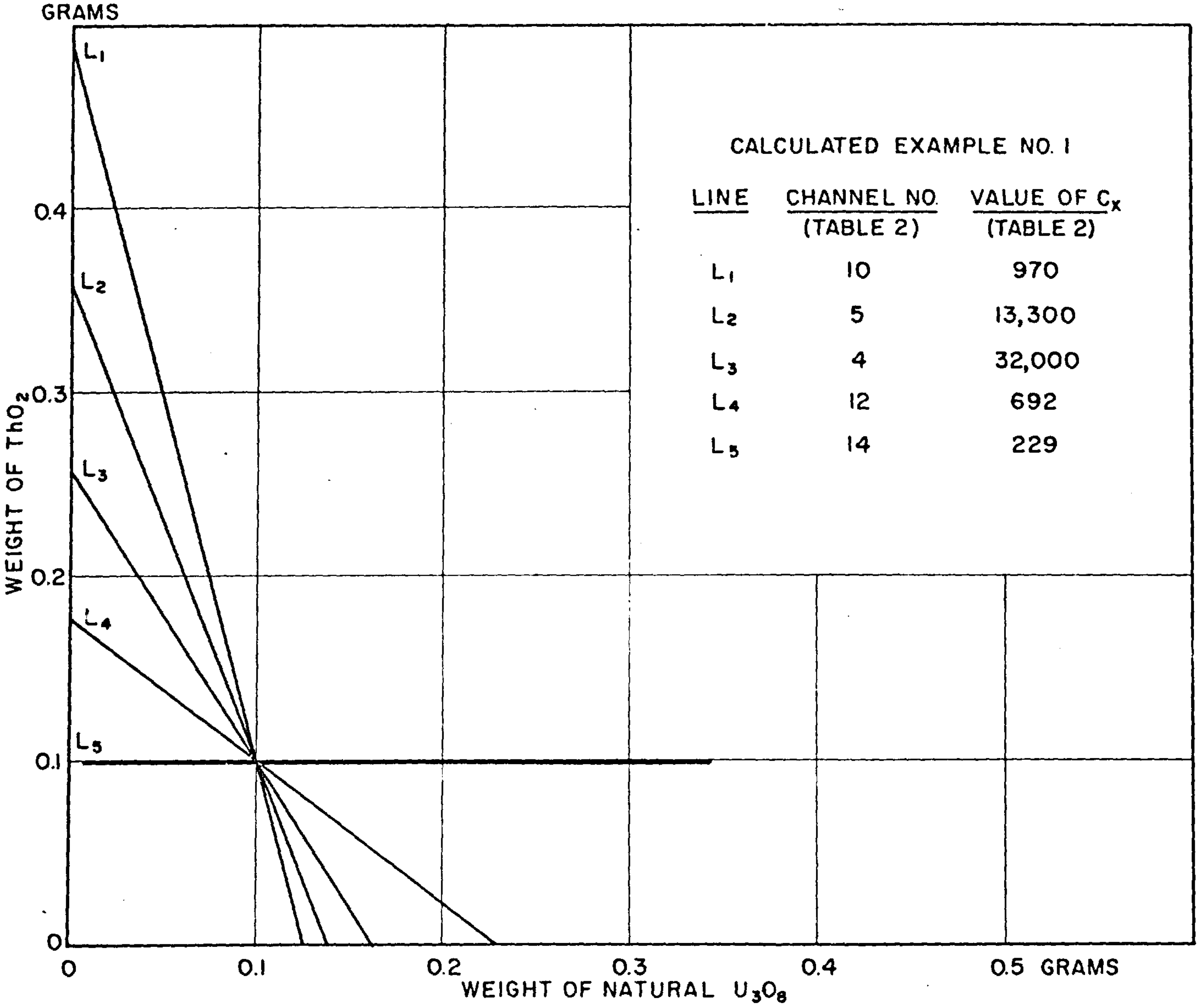
Energy Range, keV	Counts per Minute per Gram				Background, c.p.m.
	U_3O_8 (natural)	U_3O_8 (purified)	ThO_2 (natural)	K_2O	
20-40	2400	380	1015	0.21	5
40-60	4210	1090	1680	0.33	11
60-80	7140	1700	3350	0.31	17
80-100	4080	1850	2160	0.15	8
100-200	10400	1540	5790	0.44	22
200-300	9300	486	6580	0.55	19
300-400	7720	166	2440	0.36	26
400-500	1880	62	1270	0.26	18
500-600	2320	44	1450	0.20	10
600-700	2280	34	738	0.19	11
700-900	1720	55	1146	0.35	18
900-1100	1190	53	993	0.42	13
1100-1300	1170	6	254	0.36	9.4
1300-1500	772	2	198	0.59	7.3
1500-1700	460		288	0.096	6.6
1700-1900	552		161		2.6
1900-2100	152		171		1.8
2100-2300	150		219		2.3
2300-2500	51		140		1.8
2500-2700	(9)		220		1.5
over 2700			28		28.4

TABLE 2

Calculated Examples (based on Table 1)
10 min count yield

Chan. No.	Energy Range, keV	U_3O_8 (purified) (0.1 g) O	U_3O_8 (natural) (0.1 g) U	ThO_2 (natural) (0.1 g) T	K_2O (30 g) K	# 1 U + T	# 2 O + U	# 3 O + U + T	# 4 U + K	# 5 U + T + K
1	40-60	1090	4210	1680	99		5300	6980		
2	60-80	1700	7140	3350	93		8840			
3	80-100	1850	4080	2160	45		5930	8090		
4	100-300	2026	19700	12370	297	32000			20000	
5	300-500	228	9600	3710	186	13300				13500
6	500-700	78	4600	2190	117				4720	
7	700-900	55	1720	1146	105					
8	900-1100	53	1190	993	126				1320	2309
9	1100-1300	6	1170	254	108					
10	1300-1500	2	772	198	177	970		972	949	1147
11	1500-1900		1012	449	29		1012			
12	1900-2300		302	390		692			302	
13	2300-2500		51	140				191		191
14	2500-2700		(9)	220		229		229		229

Note: Weights indicate amount of oxide per 100 g sample.



CALCULATED EXAMPLE NO. 1

LINE	CHANNEL NO. (TABLE 2)	VALUE OF C_x (TABLE 2)
L_1	10	970
L_2	5	13,300
L_3	4	32,000
L_4	12	692
L_5	14	229

FIG. 3- THEORETICAL EXAMPLE FOR A MIXTURE OF ThO_2 AND NATURAL U_3O_8.

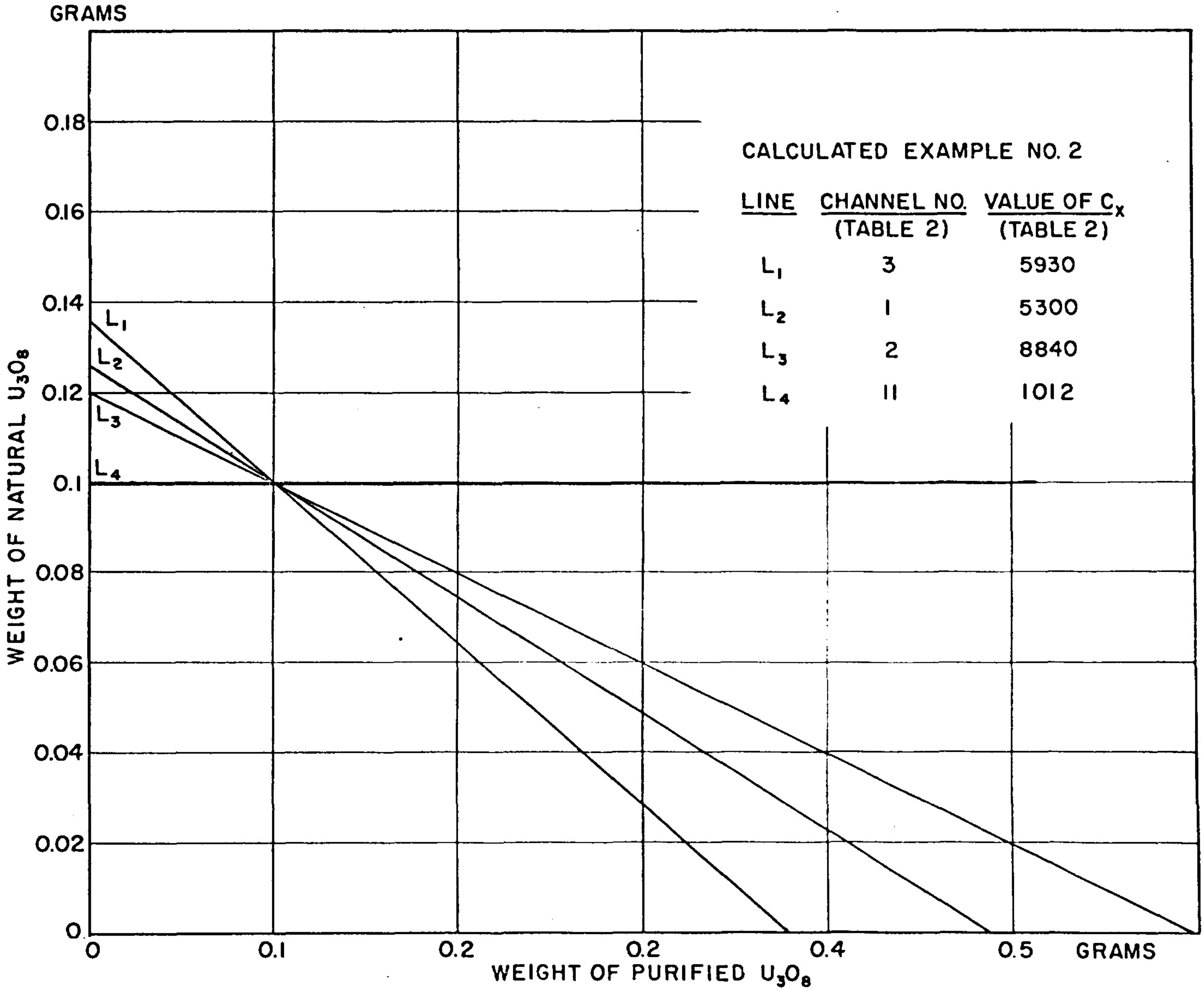
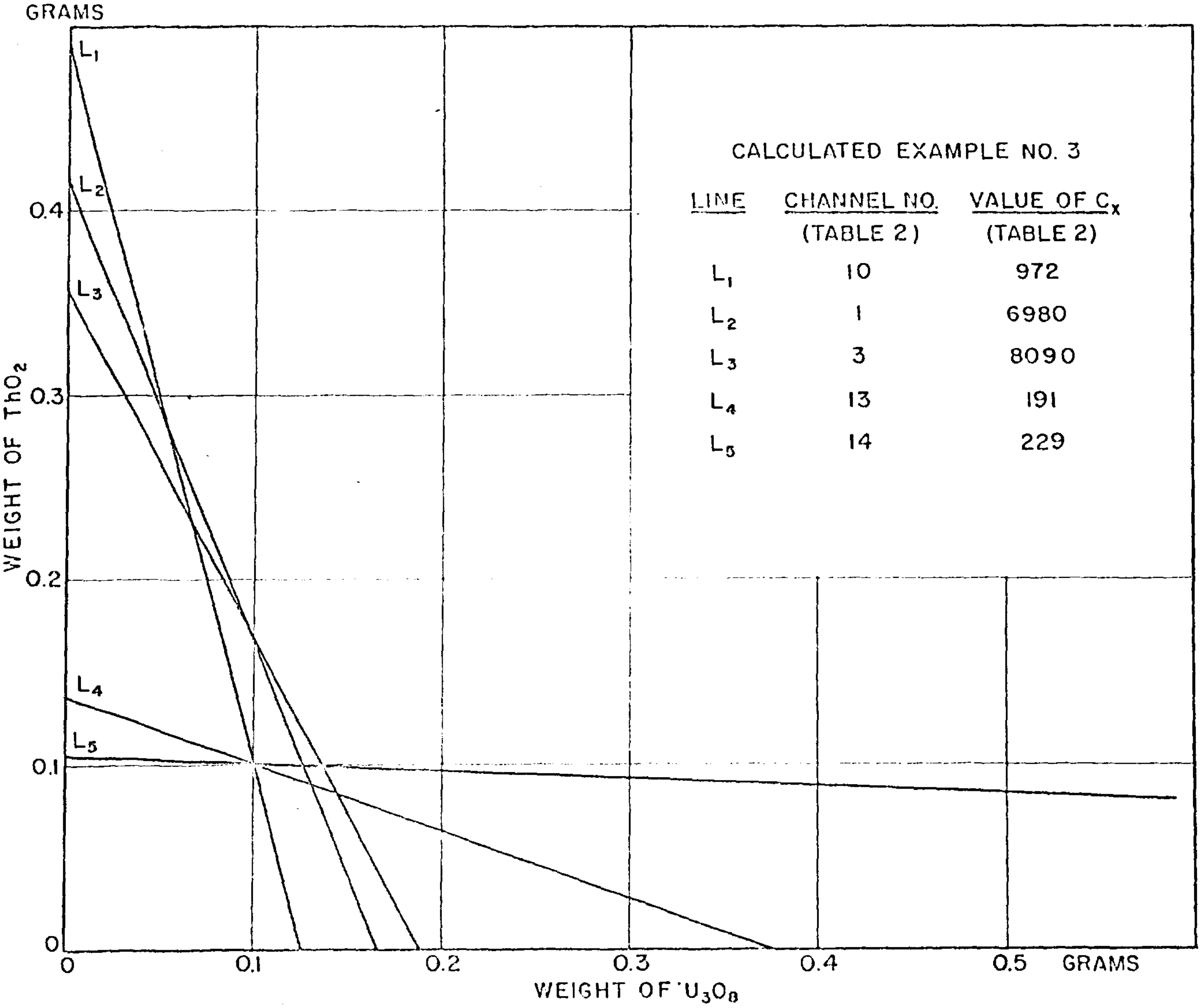


FIG. 4 - THEORETICAL EXAMPLE FOR NATURAL AND PURIFIED U_3O_8.



CALCULATED EXAMPLE NO. 3

LINE	CHANNEL NO. (TABLE 2)	VALUE OF C_x (TABLE 2)
L_1	10	972
L_2	1	6980
L_3	3	8090
L_4	13	191
L_5	14	229

FIG. 5-THEORETICAL EXAMPLE FOR A MIXTURE OF U_3O_8, ThO_2, AND PURIFIED U_3O_8 (EQUAL WEIGHTS OF EACH)

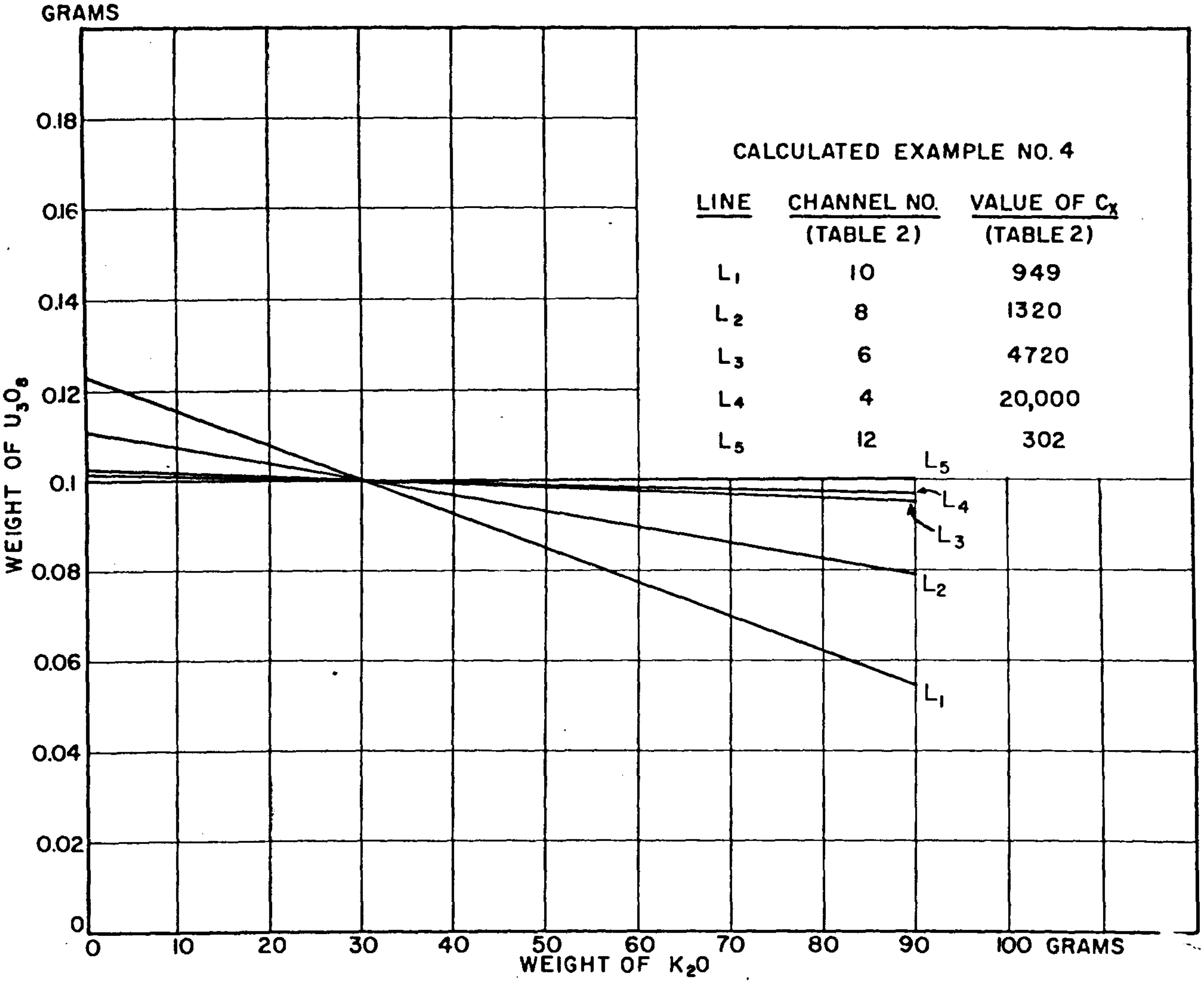
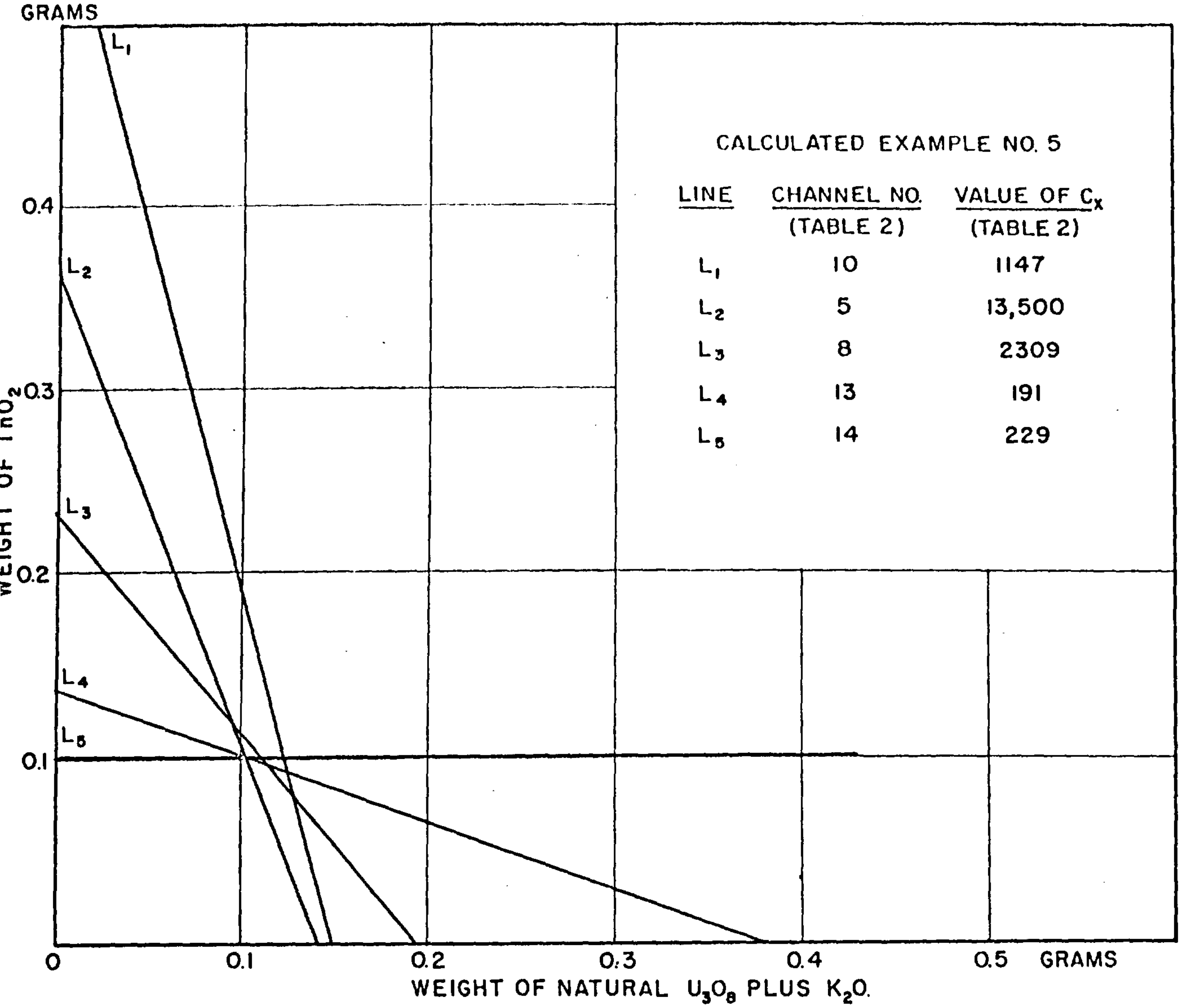


FIG. 6 – THEORETICAL EXAMPLE FOR A MIXTURE OF U_3O_8 AND K_2O.



CALCULATED EXAMPLE NO. 5

LINE	CHANNEL NO. (TABLE 2)	VALUE OF C_x (TABLE 2)
L_1	10	1147
L_2	5	13,500
L_3	8	2309
L_4	13	191
L_5	14	229

FIG. 7 – THEORETICAL EXAMPLE FOR A MIXTURE OF ThO_2 AND NATURAL U_3O_8, PLUS K_2O.

Consider the previous equation $C = au + bt$, representing the count in any spectral region resulting from two groups of radiation emitters, natural U_3O_8 and ThO_2 for example, whose weights (as the oxides) are u and t grams. A line is plotted for this equation by the intercept method, which amounts to considering the count C first to be due solely to uranium, and then solely to thorium. Points intermediate to the intercept points represent various proportions of uranium and thorium which could give the same count rate C. A similar line, having a different slope, can be obtained in another spectrum interval, if the relative sensitivity to uranium and thorium ($^a/_b$) is different. The intersection of the two lines will occur at the point representing the actual weights of u and t in that sample. In practice it is advantageous to establish the point (or small area) of intersection by means of additional lines from a total of 5 to 10 channels -- the number being limited to minimize calculation. It is evident that the spectral regions should be chosen to provide a range of lines with widely differing slopes, to render more definite the area of intersection.

The count rates in the examples shown are those which would be obtained during a 10-minute period. Figure 3 illustrates a 100 gram sample containing 0.1% U_3O_8 and 0.1% ThO_2; i.e. u and t each equal 0.1 g. Note that L_5, representing the channel of highest energy, is almost parallel to the uranium (+ radium) axis; this channel, number 14, is almost entirely above the highest energy peak emitted from the uranium series.

In the next example, Figure 4, there are equal quantities of natural uranium ore and purified uranium oxide. In this case, L_4 is parallel with the axis representing the weight of the purified uranium oxide for the same reason as in the previous example. The oxide used for this work was several months old, having reached equilibrium in so far as the short-lived daughters were concerned. The results would not apply to freshly prepared mill samples, but serve to show how departure from equilibrium in the uranium series can be determined. The contribution from the purified oxide (less the radium daughters) can be made to exceed 40 percent of the count obtained from natural uranium in a narrow region of the spectrum near 80 keV; however, the use of a narrow channel requires correspondingly better stability.

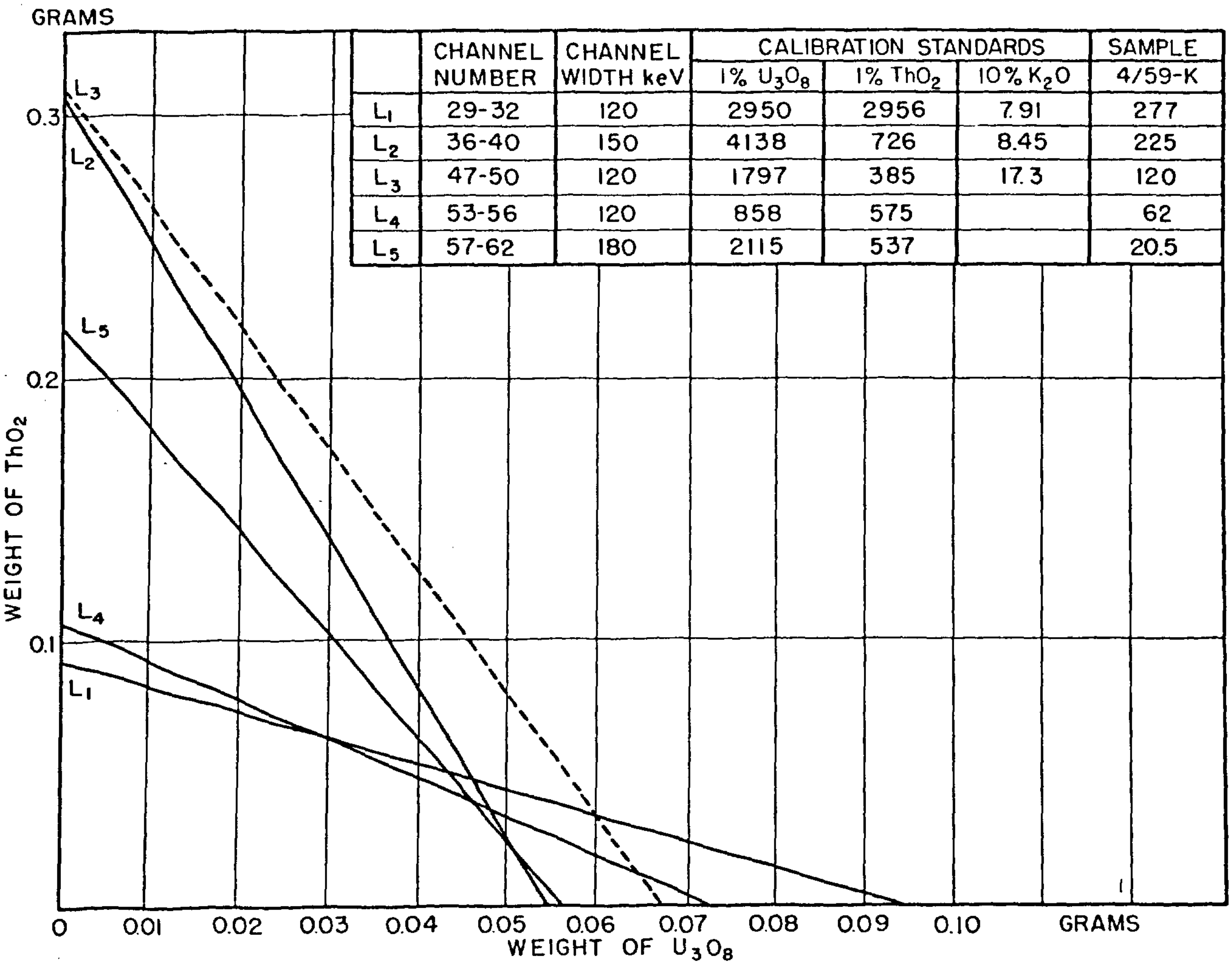
In Figure 5, a solution is obtained for natural U_3O_8 and ThO_2, considering both to be in equilibrium with their daughters. Since this fictitious sample contains, in addition, purified uranium oxide (equal in weight to the U_3O_8), the lines L_2 and L_3, representing the low energy channels, do not meet the common point of intersection of L_1, L_4, and L_5 which was obtained from the higher energy channels.

In Figures 6 and 7 the effect of potassium-40 is illustrated. By consulting these figures and Table 2, an approximate lower limit may be set to the weight of K_2O which can be detected in the presence of other activity. Thus, in Example 5, Figure 7, one can see the effect on L_1 of 30 grams of K_2O when only U_3O_8 (0.1 g) and ThO_2 (0.1 g) were considered in the solution.

Figure 8 shows an actual solution of a synthetic ore sample (No. 4/59-K) containing 10% K_2O, 0.05% ThO_2 and 0.05% U_3O_8. The effect of the potassium was negligible, except in the region around 1.46 MeV represented by L_3. A solution was obtained from the intersection of the four remaining lines: 0.046 gram U_3O_8 and 0.045 gram ThO_2 per 100 gram sample. The discrepancy in L_3 was attributed to potassium. Calculation gave the K_2O content as 9.8 grams in a 100 gram sample.

When more than two nuclide groups are present in detectable quantities in a sample, a solution should be obtained by working down the gamma-ray spectrum from the highest energy region, considering two groups at a time.

Solutions for several actual ore samples are summarized in Table 3; they are within the range of agreement of other methods of analysis. The graphical solutions for two typical samples are shown in Figures 9 and 10.



	CHANNEL NUMBER	CHANNEL WIDTH keV	CALIBRATION STANDARDS			SAMPLE
			1% U_3O_8	1% ThO_2	10% K_2O	4/59-K
L_1	29-32	120	2950	2956	7.91	277
L_2	36-40	150	4138	726	8.45	225
L_3	47-50	120	1797	385	17.3	120
L_4	53-56	120	858	575		62
L_5	57-62	180	2115	537		20.5

FIG. 8 – SYNTHETIC SAMPLE CONTAINING URANIUM, THORIUM AND POTASSIUM.

TABLE 3

Analysis of Typical Ore Samples (percentage of weight)

Sample No.	Chemical		Radiometric (Beta - Gamma)		Graphical (Gamma Spectrometer)	
	U_3O_8	ThO_2	U_3O_8	ThO_2	U_3O_8	ThO_2
266	0.20	0.13	0.17	0.17	0.19	0.15
267	0.25	0.07	0.20	0.17	0.24	0.07
269*	0.11	0.06	0.14	--	0.13	0.05
362**			0.051	0.085	0.05	0.08
365			0.15	--	0.13	0.06
393			0.077	0.054	0.07	0.06
397			0.034	0.04	0.03	0.05

* Graphical solution shown in Figure 9.

** Graphical solution shown in Figure 10.

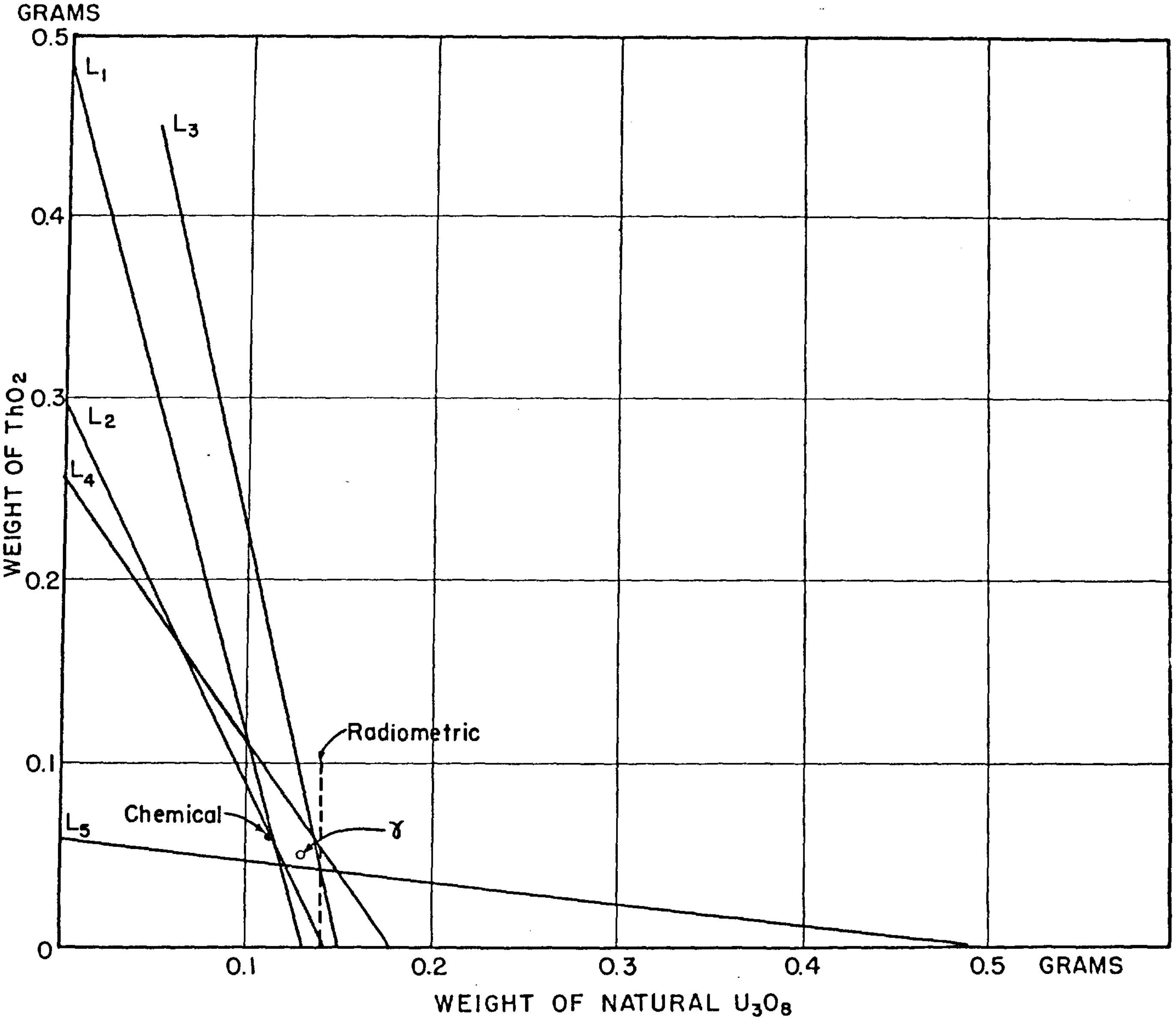


FIG. 9 - ORE SAMPLE NO. 269.

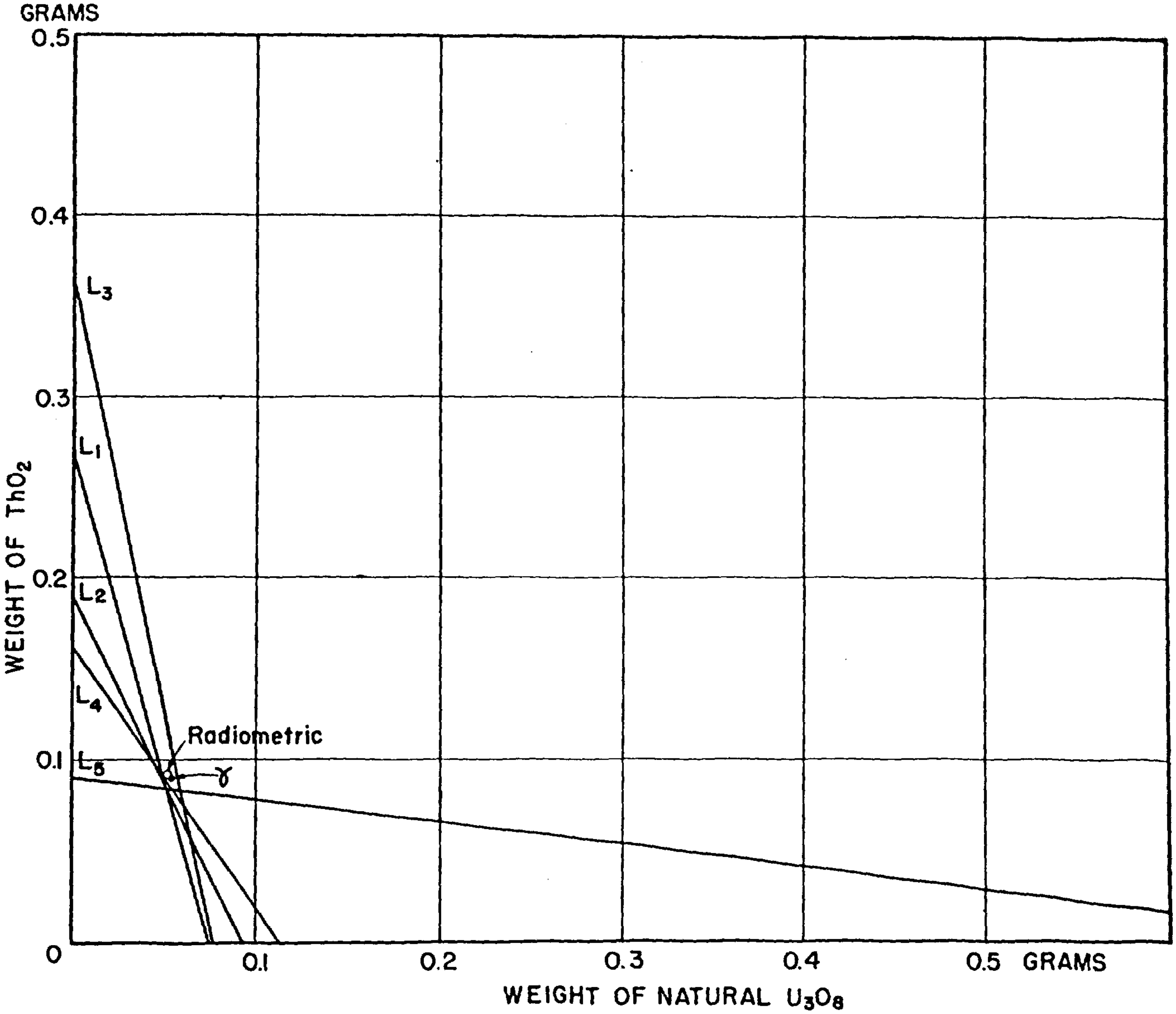


FIG. 10-ORE SAMPLE NO. 362

CONCLUSIONS

The time required for the counting and calculation of a prepared sample is generally about twenty minutes; however, because the calculations remain somewhat complex, the method would not be preferable to the usual radiometric methods except in a few instances: (a) when more than two radioactive components are present in a sample; (b) when the abundance of two components differs widely, for example, a thorium to uranium ratio greater than 10:1; (c) when the abundance of the components is low; (d) as a non-destructive method of analysis (crushing of sample not required).

Additional time is required periodically to check the calibration, but this can be minimized by reducing sensitivity variations. Once adequate regulation of critical voltages has been achieved, the most serious factor affecting sensitivity is temperature change around the photomultiplier tube. The latter should be controlled to within 1 centigrade degree. The walls of the lead castle shielding the sample should be lined with a light metal to reduce the lead X-ray peak at 73 keV.

To enable very small samples to be analysed by this method, and to improve the sensitivity through better sample geometry, a well-type detector could be employed as was done by Hurley(6). With a small sample, the effect of self adsorption would be reduced considerably below 100 keV. The well detector would not have as good a resolution, however, as has the cylindrical crystal used here.

ACKNOWLEDGMENTS

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APPENDIX

Sample Calculation

Solution of example No. 1 - the graph is shown in Figure 3.

In channel 10, Table 2, Cx equals 970 counts for 10 minutes. Table 2 indicates that 0.1 gram of natural ThO_2 yields 198 counts in 10 minutes and that 0.1 gram of natural U_3O_8 yields 772 counts in 10 minutes.

Cx could have resulted from $\frac{970}{198} \times 0.1 = 0.49$ gram ThO_2

or from $\frac{970}{772} \times 0.1 = 0.126$ gram U_3O_8.

L_1 in Figure 3 is obtained by plotting the latter two weights on the appropriate axes and then joining the points with a straight line. Similarly L_2, L_3, ... are plotted from values obtained in channels 5, 4, ...

The lines intersect within a small area (a point in this idealized case) indicating the required weights of ThO_2 and U_3O_8 which contribute to the total count observed.

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