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James Robert Lawrence
Union College - Schenectady, NY

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THE DETERMINATION OF THE RATIOS U^{234}/U^{238} AND Th^{228}/Th^{232} AS LEACHED FROM STORM KING GRANITE

by

James Robert Lawrence UC 1964

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By James R Lawrence

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THE DETERMINATION OF THE RATIOS U^{234}/U^{238} AND Th^{228}/Th^{232} AS LEACHED FROM STORM KING GRANITE

HISTORICAL

In nature there are three major decay series that involve naturally occuring uranium and thorium as parent nuclides. Two of the three series; U-238, Th-232 and U-235; are shown in figure I. Of the three series two, U-238 and the Th-232 series, are examined in this study. This is because the amount of U-235 in nature is very small relative to the amount of U-238 and Th-232.

This study is concerned with the presence of U-238 and Th-232 and their uranium, thorium and radium daughter products in the silicic intrusive rock, Storm King Granite. Uranium and thorium have large ionic radii and high coordination numbers. For this reason they are concentrated in accessory minerals rather than in normal rock forming minerals. (7) (Thurber) Since accessory minerals don't form until the temperature and pressure are low enough uranium and thorium are concentrated in crustal rocks. The earth is generally more acidic in its crust. Correspondingly uranium and thorium are more concentrated in the more acidic rocks such as granite. (1) (Adams, Table I) Silver (5) has found the following distribution of uranium and thorium in granite rocks. "The primary distribution of the uranium and thorium series in granite rocks can be generalized in having three types of sites:

Figure I

Natural Decay Series

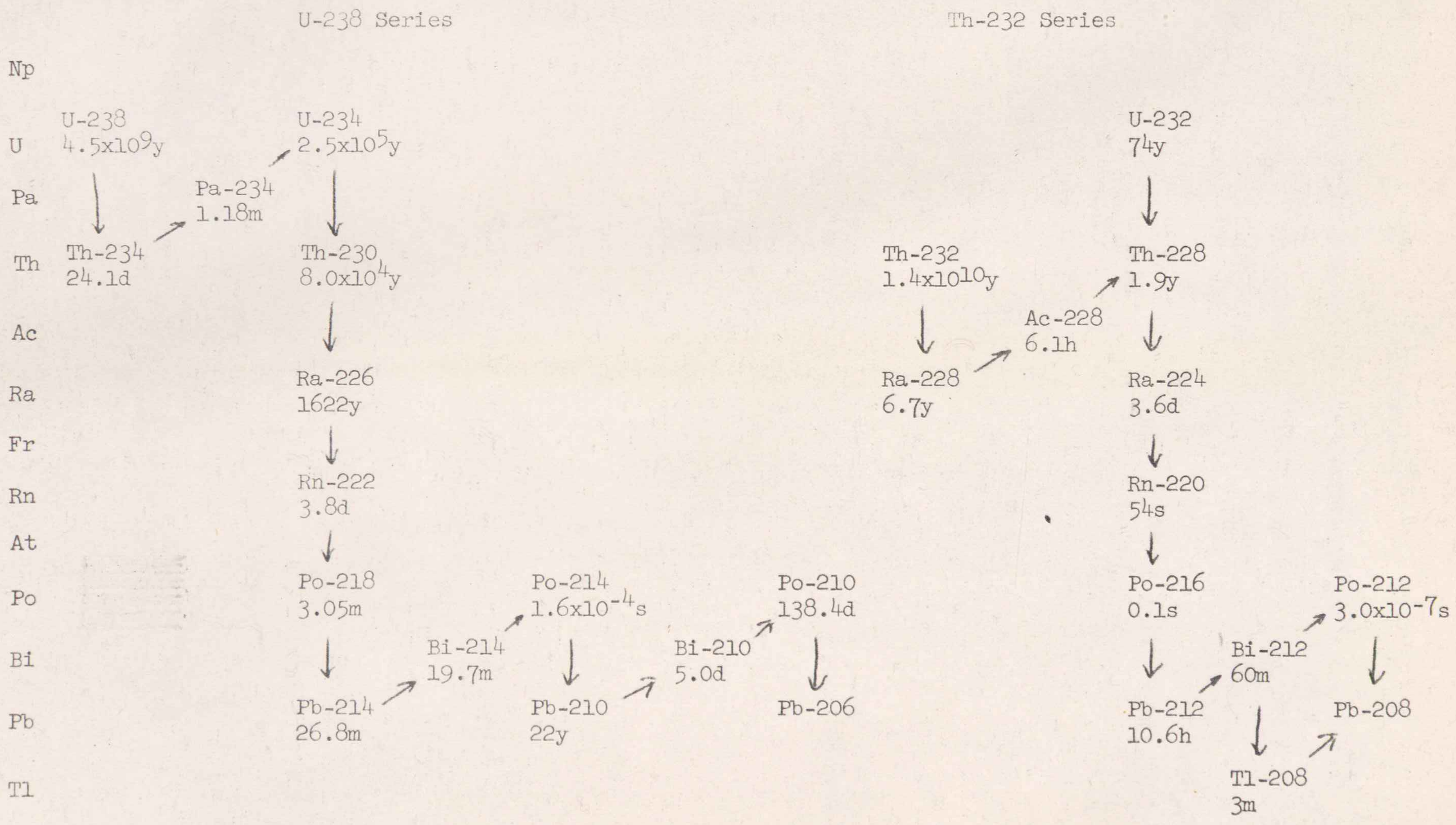


Table I

Uranium and thorium in igneous rocks ⁄

Rock	Thorium (ppm)	Uranium (ppm)	Th/U
Silicic intrusive	1-25	1-6	2-6
Silicic extrusive	9-25	2-7	4-7
Basic intrusive	0.5-5	0.3-2	3-4
Basic extrusive	0.5-10	0.2-4	3-7
Ultrabasic	low	0.001-0.03	
Alkaline series		0.1-30	
Silicic pegmatite	1-2	1-4	0.4-1.5

⁄ Adams (1)

[1] minor accessory minerals in which the U^{+4} and Th^{+4} are structurally acceptable in concentrations higher than the average concentration of the total rock system; [2] dispersed low-level concentrations in major phases in the rock; and [3] an apparent localization on a microscopic to submicroscopic scale along fractures and grain boundaries. In more than 100 igneous rocks of various types, site [1] is commonly the most important while [2] and [3] may be alternated in relative importance. We have found a definite correlation between the weathering of granites and the dispersal of their contained radioactivity along permeable fractions. The mechanisms of dispersal are, however, quite complex, and are not confined solely to the weathering processes."

Storm King Granite is a rock of PreCambrian age found in south eastern New York State near Bear Mountain. It can be placed in the following series of events in geologic history. There was sedimentation in the Grenville and Huronian time. There was then a period of metamorphism in the Grenville. A period of vulcanism occurred which resulted in a huge batholith under the Bear Mountain area. One of the protrusions of this batholith is believed to have resulted in the formation of Storm King Granite. Storm King Granite was formed either from melted sediments or intruded magma. Storm King Granite is 1000 million years old. After the formation of Storm King Granite there were two effects on the granite. 350 million years ago metamorphism associated with the Taconic Disturbance altered the rocks slightly. Since that time the only effect has been the possibility of disturbance by ground water and weathering. (2) (Berkey) and (8) (Thurber)

Uranium has two oxidation states in nature and thorium has one. Uranium in solution in nature exists in the state U^{+6} as complexes of UO_2^{+2}. Some of the more important ones are the carbonate complexes $UO_2(CO_3)_3^{-4}$ and $UO_2(CO_3)_2(H_2O)_2^{-2}$ which exist between a pH of 6 and 9. Uranium exists in fresh water bodies and in the ocean in such complexes. The oxidation state of uranium in rocks is not known for sure but it is most probably +4. Thorium exists in nature only as Th^{+4} in rocks. It forms few strong complexes and is easily precipitated in saline solution. Thus thorium is not very abundant in sea water but precipitates onto the continental shelves. (8) (Thurber)

The two parent nuclei U-238 and Th-232 exist theoretically in secular equilibrium with their daughter products. That is, an activity ratio of a daughter product to its parent should be unity in a system allowed to come to equilibrium. Thus if undisturbed the activity ratios Th^{228}/Th^{232} and U^{234}/U^{238} should be unity in the granite and in the water passing over the granite. Thurber (6) (7) has studied the activity ratio U^{234}/U^{238} as found in fresh and salt water bodies on the earth. He has also studied the ratio in marine carbonate deposits. He has found the ratio to be quite different from unity, usually greater than one (8) (Thurber, Table II). Since the uranium and thorium in solution and sedimentary rocks have as a major source igneous rock basic research is needed on the extraction of uranium and thorium and their various activity ratios from an igneous rock. This study is an attempt

Table II

Rock	U^{234}/U^{238} in water flowing over the rock
Granite	0.8-8
Sandstone	1.21
Monzanite	1.14
Granodionite	1.32
Alkali Basalt	1.76
Paleozaic Sediments	1.98
Limestone	6.35

(8) (Thurber)

to start a basic laboratory study on the extraction of uranium, thorium and radium from rock forming minerals.

The radionuclides U-238, Th-234, U-234, Th-230, Ra-226, Th-232, Ra-228, Th-228 and Ra-224 are of most interest. A discussion of some of these nuclides and their various activity ratios can be found in Thurber (7). The activity ratios of primary interest here are U^{234}/U^{238} and Th^{228}/Th^{232}. Since U-234 is a daughter produ ct of U-238 we must understand what happens between the decay of U-238 and the formation of U-234. Chemical bond energies are on the order of one to five ev. If a nuclear particle leaves the nucleus with an energy of more than a hundred Kev, the kinetic energy imparted to the nucleus is in excess of the chemical energies of the molecule in which it is found (3) (Friedlander). When a four Mev alpha particle leaves a U-238 nucleus, it not only strips the nucleus of many of its electrons, but it imparts a recoil energy of some 30 Kev. The nucleus then loses this energy by breaking its bonds, and destroying the lattice around it by collision with its neighboring atoms. The nucleon is now in a lattice defect of its own making, and its chemical character has changed. Even the chemical character of U-234 may be different from its parent if the process of decay has catalyzed the oxidation of the nuclide by stripping it of electrons. (7) (Thurber) Daughter nuclides of alpha emitting parents are thus seen to be physically more available to weathering than the parent owing to their location in a defective lattice, especially if they are near the surface of the minerals. They may be chemically more or less available, depending on the

characteristics of the nuclide and the leaching solutions. A similar argument may be put forth for thorium except that oxidation of thorium could not take place since it has only one oxidation state. We may note however that the daughter Ra-228 is a substance easily soluble in aqueous solutions which could have its own effect on the Th^{228}/Th^{232} ratio.

Thurber has proposed that a comparison of the Th^{228}/Th^{232} and the U^{234}/U^{238} ratios as extracted from Storm King Granite could suggest what happens in the time lapse between the two components of the ratios. Three parameters are expected to be important in affecting these ratios. These three are recoil due to decay, oxidation state, and the chemistry of radium. Let us compare the two decay schemes involving the ratios.

$$\text{U-238} \xrightarrow[\alpha]{} \text{Th-234} \xrightarrow[\beta^-]{24.1\text{d}} \text{Pa-234} \xrightarrow[\beta^-]{1\text{m}} \text{U-234} \xrightarrow[\alpha]{2.5 \times 10^5\text{y}}$$

1. Decay particles - 1 alpha, 2 betas
2. Immobile intermediates - i.e. thorium-234 is short lived.
3. The oxidation state of uranium can change.

$$\text{Th-232} \xrightarrow[\alpha]{} \text{Ra-228} \xrightarrow[\beta^-]{6.7\text{y}} \text{Ac-228} \xrightarrow[\beta^-]{6\text{h}} \text{Th-228} \xrightarrow[\alpha]{1.9\text{y}}$$

1. Decay particles - 1 alpha, 2 betas
2. Mobile intermediates, i.e. radium is soluble in most aqueous solutions and has a half life of 6.7 years.
3. The oxidation state can not change for thorium.

Here are the proposals set forth by Thurber (8). Thurber assumes that parent and daughters are undisturbed and in secular equilibrium in the rock. If the recoil is the important thing in making the daughters extractable the U^{234}/U^{238} should be similar to Th^{228}/Th^{232}. If a change in oxidation state is important the U^{234}/U^{238} should be higher than Th^{228}/Th^{232}. If the displacement of radium by water in the crystal lattice is important the Th^{228}/Th^{232} ratio should be higher than U^{234}/U^{238}.

Very little work has been done in leaching thorium and uranium from igneous rocks and measuring their isotope ratios. Thurber made one or two leaches on granite samples with sodium carbonate and hydrochloric acid and found a U^{234}/U^{238} ratio greater than one. (7) (Thurber) Therefore this study is intended to get a good start on leaching uranium and thorium from Storm King Granite and measuring their activity ratios. The variety of solutions and conditions of leaching are to be extended as far as possible in the time available for the study. Ratios will be measured at Union College and spiked samples will be sent to Lamont Geological Observatory of Columbia University for further measurement of the ratios.

APPARATUS

1. Beta Counter

Anton type pancake Geiger counter with anticoincident ring and electronic circuiting constructed by the electronics shop of Lamont Geological Observatory.

2. Alpha Counter

Tank type scintillation counter with Dumont 6912 Phototube coated with powdered ZnS phosphor. Baird Atomic Multiscaler II, Model 132, Timer Model 960R.

3. Alpha Spectrometer

Ortec 5BFF45-60 silion barrier detector, Ortec 101-201 preamp-amplifier system, RIDL 3416 400 channel analyzer.

SEPARATION TECHNIQUES

The following scheme was used to separate radium, uranium and thorium.

Rock — 250 gms.

↓ Leach — 500 ml. 0.5 Na_2CO_3, 2N HCl, 2N H_2SO_4

Solution	
Spiked	Unspiked

The solution is split and one half is spiked with U^{232} in equilibrium with its daughter products.

↓ NH_4OH to pH-7 → Ra^{+2} and soluble metal ions

$Fe(OH)_3$ and coprecipitates

If Na_2CO_3 is used as a leach the carbonate must be destroyed with HCl and iron must be added in order to precipitate $Fe(OH)_3$

↓ conc. HCl

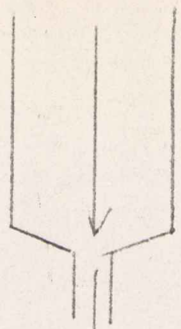
Solution Adjusted to 8N in HCl

↓ Isopropyl Ether — Extracts excess iron

Solution in 8N HCl

↓

Continued



Anion Resin Column Dowex I-8

100-200 mesh 17cc

1. Wash with 8N HC1
2. Pour through the solution
   6N HC1
3. Wash with 8N NC1
4. Wash with 0.1N HC1

0.1N HC1 ↙ ↘ 6N HC1

Left branch (0.1N HC1):

Solution containing thorium, silicon and aluminum

↓ Add Iron, NH_4OH to pH-7

$Fe(OH)_3$ and Coprecipitates

↓ 3N NaOH and heat — Waste →

$Fe(OH)_3$, Thorium

↓ Concentrated HNO_3

Solution adjusted to 6N in HNO_3

↓

Continued

Right branch (6N HC1):

Solution containing uranium, iron, copper, etc.

↓ Isopropyl ether to extract iron

8N Solution

↓ Evaporate

Dry deposit

↓ 6N HNO_3 evaporate

Dry deposit

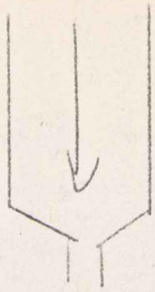
↓ 1-2 ml distilled water pH3-4

Solution

↓ TTA 1-2Ml, shake centrifuge separate

Evaporate

*TTA on a Plancet



Cation column, Dowex 50-8
100-200 mesh 10cc

Waste → Iron and others

1. Wash with 6N HNO_3
2. Pour through the sample
3. Wash with 6N HNO_3
4. Wash with 50ml 0.75m oxalic acid

0.75m
Oxalic Acid

↓

Solution containing
Thorium

↓ Add 5-10 ml of 60% $HC10_4$ and evaporate at a high temperature

Dry Deposit

↓ 6N HNO_3 and evaporate

Dry Deposit

↓ 0.001 N HNO_3 pH 1-2
1-2 ml

1-2 ml Solution

↓ *TTA, shake, centrifuge, separate

Evaporate TTA on
a plancet

* TTA = 4, 4, 4-Trifluoro-1-(2-thienyl)-1, 3-butanedione

TABLE III

DATA

Sample	Time hr.	Spike ml.	U^{238}/U^{232}	U^{238} dpm	U^{238} ppm	Th^{232}/Th^{228} spike	Th^{232} dpm	Th^{232} ppm	Th^{230} dpm	Ra^{226} dpm	Th/U	U^{234}/U^{238}	Th^{230}/U^{238}	Th^{228}/Th^{232}	Th^{230}/Th^{232}
1C			0.72		.043					5.2		0.97			
1CS	6.0	2.0	±.06	8±1	±.005					±0.4		±.08			
2C			1.7		.097					2.6		0.94			
2CS	12.0	2.0	±0.1	18±1	±.005					±0.2		±.07			
3C			2.2		0.13					2.5		0.95			
3CS	24.0	2.0	±0.1	24±2	±.01					±0.1		±.04		3.4±0.7	0.27±.09
4A		10.0	2.1									1.10			
			±0.2	110±10								±.08			
14C			1.06		0.10	0.6		0.34	6		3.4	0.94	0.32	3.3±0.3	0.52±.07
14CS	18.0	3.5	±.07	19±2	±.01	±0.2	12±4	±.12	±2		±1.4	±.05	±12	5.0±0.2	0.47±.04
19C			0.93		.076	1.0		0.44	8		5.8	0.78	0.58	2.4±0.2	0.38±.06
19CS	21.0	2.9	±.09	14±2	±.007	±0.6	16±10	±.32	±6		±4.6	±.07	±.50	3.4±0.3	0.53±.08
20C			1.17		0.076	0.4	4.8	0.12	3.0		1.6	1.02	0.22	3.4±0.4	0.57±.11
20CS	21.0	2.2	±0.12	14±2	±.007	±0.2	±2.4	±.06	±1.6		±0.8	±.10	±.12	4.6±0.5	0.60±.11

TABLE III (Continued)

Sample	Time hr.	Spike ml.	$\frac{U^{238}}{U^{232}}$	U^{238} dpm	U^{238} ppm	$\frac{Th^{232}}{Th^{228}}$ spike	Th^{232} dpm	Th^{232} ppm	Th^{230} dpm	Ra^{226} dpm	$\frac{Th}{U}$	$\frac{U^{234}}{U^{238}}$	$\frac{Th^{230}}{U^{238}}$	$\frac{Th^{228}}{Th^{232}}$	$\frac{Th^{230}}{Th^{232}}$
12H			24	297	1.6	11	138	3.8	28		2.4	0.86	0.11	0.97±.01	0.21±.01
12HS	19.0	2.3	±3	±25	±0.1	±2	±30	±0.8	±8		±0.8	±.03	±.06	1.06±.01	0.23±.01
13H				114	0.6							0.83			
13HS	19.8	2.6	8±1	±18	±0.1							±.03		1.07±.03	0.25±.01
18H			7.6	94	0.51	14	174	4.8	36		9.4	0.86	0.38	0.97±.04	0.22±.01
18HS	18.5	2.3	±0.4	±5	±.02	±9	±120	±3.6	±24		±6.0	±.03	±.28	1.05±.02	0.21±.01
16S			1.6	21	0.11		118	3.2	24		28	*0.54	1.14	0.90±.04	0.20±.02
16SS	18.5	2.4	±0.1	±2	±.01	9±7	±90	±2.4	±18		±24	±.03	±.08	1.01±.03	0.25±.01
17S			8.4	146	0.79		162	4.6	36		5.8	0.92	0.24	0.93±.02	0.21±.01
17SS	18.8	3.3	±0.6	±12	±.07	9±4	±70	±2.2	±16		±2.8	±.03	±.12	1.04±.02	0.23±.01
21					4.57			31			6.78	0.95	0.99		0.43
					±2%			±2%			±4%	±.02	±.04		±.02

*Very Poor Spectra

Data

$1 \mu g\ U^{238} = 0.74$ dpm

$1 \mu g\ Th^{232} = 0.14$ dpm

Samples

250 gm of Storm King Granite

500 ml of Leach Solution

Leach Solutions

C = 0.5N Na_2CO_3

CS = 0.5N Na_2CO_3 with spike added

4A = 4C, 4CS, 5C, 5CS, 6C, 6CS, 7C, 7CS combined

H = 2.0N HC1

HS = 2.0N HC1 with spike added

S = 2.0N H_2SO_4

SS = 2.0N H_2SO_4 with spike added

21 = A complete dissolving of a 20gm sample of Storm King Granite

Spike

The spike contains 2.7 dpm/ml of U^{232} and its daughter products in secular equilibrium.

Calculations

Sample 12H & 12HS

$\frac{U^{234}}{U^{238}} = 0.86 \pm .03$ taken from Graph 12HSU

$\frac{Th^{228}}{Th^{232}} = 0.97 \pm .01$ taken from Graph 12H Th

$\frac{Th^{228}}{Th^{232}} = 1.06 \pm .01$ taken from Graph 12HS Th

$\frac{Th^{230}}{Th^{232}} = 0.23 \pm .01$ taken from Graph 12HS Th

$\frac{U^{238}}{U^{232}} = 24 \pm 3$ taken from Graph 12HS U

U^{238} dpm

$$\text{dpm} = \text{Spike} \times \text{No. of ml. of spike} \times \frac{U^{238}}{U^{232}} \times 2^*$$

*Sample was split in two, a correction of two is necessary.

$$\text{dpm } U^{238} = 2.7\,(2.3)\,(24)\,(2) = 297 \text{ dpm}$$

U^{238} ppm

$$\text{ppm} = \frac{\text{dpm}}{\frac{\text{dpm}}{\mu\text{g}}} \times \frac{1}{\text{Wt. of sample in } \mu\text{g}} \times 10^6$$

$$\text{ppm} = \frac{297}{0.74} \times \frac{1}{2.5 \times 10^8} \times 10^6 = 1.6 \text{ ppm } U^{238}$$

$$\frac{Th^{232}}{Th^{228}} \text{ spike}$$

$$\frac{Th^{232}}{Th^{228}} \text{ spike} = \frac{\text{No. of Counts in } Th^{232} \text{ spiked sample peak}}{\text{No. of Counts in } Th^{228} \text{ spiked peak} \times \dfrac{\dfrac{Th^{228}}{Th^{232}} \text{ spike} - \dfrac{Th^{228}}{Th^{232}} \text{ unspiked}}{\dfrac{Th^{228}}{Th^{232}} \text{ unspiked}}}$$

$$= \frac{9699}{10307 \times \dfrac{1.06 - 0.97}{1.06}}$$

$$= \frac{9699}{10307 \times \dfrac{0.09}{1.06}}$$

$$= \frac{9699}{875} = 11$$

$$Th^{232} \text{ dpm}$$

$$\text{dpm} = \text{Spike} \times \text{No. of ml of spike} \times \frac{Th^{232}}{Th^{228} \text{spike}} \times 2$$

$$\text{dpm} = 2.7 \times 2.3 \times 11 \times 2$$

$$\text{dpm} = 138$$

$$Th^{232} \text{ ppm}$$

$$\text{ppm} = \frac{\text{dpm}}{\dfrac{\text{dpm}}{\mu g}} \times \frac{1}{\text{Wt. of sample in } \mu g} \times 10^6$$

$$\text{ppm} = \frac{138}{0.14} \times \frac{1}{2.5 \times 10^8} \times 10^6$$

$$\text{ppm} = 3.8$$

Th^{230} dpm

$$Th^{230}\ dpm = Th^{232}\ dpm \times \frac{Th^{230}}{Th^{232}}$$

$$Th^{230}\ dpm = 138 \times 0.22$$

$$Th^{230}\ dpm = 28$$

Th/U

$$\frac{Th}{U} = \frac{Thppm}{Uppm}$$

$$\frac{Th}{U} = \frac{3.8}{1.6} = 2.4$$

$\frac{Th^{230}}{U^{238}}$

$$\frac{Th^{230}}{U^{238}} = \frac{Th^{230}\ dpm}{U^{238}\ dpm} = \frac{28}{297}$$

$$\frac{Th^{230}}{U^{238}} = 0.11$$

Error

$$\sigma\% = \frac{\sqrt{\text{Counts in a peak}}}{\text{Counts in a peak}}$$

$$\sigma\% = \frac{\sqrt{S}}{S}$$

SUMMARY AND DISCUSSION

Model

Area of Exposed Uranium & Thorium	$\frac{U^{234}}{U^{238}} < 1$ $\frac{Th^{228}}{Th^{232}} \sim 1$ $\frac{Th^{230}}{U^{238}} < 1$ $Th^{230}/Th^{232} \sim 0.23$	Area along grain boundaries and fractures
Area of Buried Uranium & Thorium	$\frac{U^{234}}{U^{238}} = 1$ $\frac{Th^{228}}{Th^{232}} = 1$ $\frac{Th^{230}}{U^{238}} = 1$ $\frac{Th^{230}}{Th^{232}} \sim 0.4$	Area of accessory minerals

In Table II it is noted that the majority of water samples contain a $\frac{U^{234}}{U^{238}}$ greater than unity. If we take note of the $\frac{U^{234}}{U^{238}}$ extracted by the various leaches it can be seen that they are less than unity. The total analysis shows a $\frac{U^{234}}{U^{238}}$ less than unity. The assumption must be made that the granite is deficient in U^{234}. Secular equilibrium does not exist between the parent U^{238} a
and its daughters.

The Th^{232} is assumed to be in secular equilibrium with its daughter because of the short half life of Th^{228} and the results of the acid leaches.

The most outstanding result obtained was the Th^{228}/Th^{232} leached by carbonate solution. The unspiked samples showed a ratio from 2.4 to 3.4.

Th^{228} was definitely leached in preference to Th^{232}. This is further emphasized by the Th^{230}/Th^{232} leached by the carbonate solution. The Th^{230}/Th^{232} leached by the carbonate solution is consistantly higher than that leached by the acid solution. It must be noted that the carbonate solution is a weak leach compared to the acid leaches. This may be noted in the columns headed Th^{232}dpm and Th^{232}ppm in Table III. The interpretation is this. The Th^{228}/Th^{232} is high because Th^{228} is leached in preference to Th^{232} by the weak leach Na_2CO_3. This means that Th^{228} is more exposed than Th^{232}. This may be due to one of two things. The decay of Th^{232} produces Ra^{228} which becomes Th^{228} in a defective lattice thus making it more available for leaching. Also the Ra^{228} formed could move out of its position due to ground water. On decaying to Th^{228} it is removed from its original sight and thus is more exposed to leaching. The over-all Th^{228}/Th^{232} of the whole rock is expected to be close to unity.

The Th^{230}/Th^{232} in the over-all rock is 0.43. The carbonate leaches gave Th^{230}/Th^{232} ratios generally higher than 0.43. The acid leaches gave results lower than 0.43. In light of Silver's (5) statements the confusion may be settled by the use of a model. There are two general sights for uranium and thorium, exposed sights and buried sights. This is the interpretation. The Th^{230}/Th^{232} in the exposed sights is ~ 0.23. The Th^{230}/Th^{232} in the buried sights is ~ 0.4. The buried sight is a larger area. The carbonate, a weak leach, leaches from the exposed area but leaches Th^{230} in preference

to Th^{232} since Th^{230} is a daughter product of U^{238}. The acids, a strong leach, leach the exposed area heavily, leaching a Th^{230}/Th^{232} ratio of ~ 0.23. The over-all Th^{230}/Th^{232} is a combination of both areas and since the buried sight is larger the ratio is closer to that of the buried sight.

As was stated earlier there is an over-all deficiency of U^{234} in the Storm King Granite. Carbonate is a stronger leach for uranium than thorium since uranium forms strong carbonate complexes. However, the acid leaches are stronger than the carbonate leaches as indicated by the columns headed U^{238}dpm and U^{238}ppm in Table III. The uranium ratios are not nearly as revealing as the thorium ratios since the ratios don't vary as much from weak leaches to strong leaches. But if the model is followed the uranium ratio data may be explained. This is the interpretation. The U^{234}/U^{238} in the exposed sights is less than unity ~ 0.85. The U^{234}/U^{238} in the buried sights is unity. The carbonate, a weak leach, leaches the exposed sights but taking U^{234} in preference to U^{238} a ratio greater than 0.85 is obtained. The acid leaches leach the exposed area more fully thus giving U^{234}/U^{238} ~ 0.85. The over-all analysis gets both buried and exposed sights and thus gives $\frac{U^{234}}{U^{238}}$ close to unity but less than unity.

There is further evidence for believing that Storm King Granite is a heavily weathered rock. The Th^{230}/U^{238} ratios found in the leaches are less than unity. The Th^{230}/U^{238} ratio in the whole rock is closed to unity. This indicates that Th^{230} is deficient in the exposed sights of the rock which

is expected since U^{234} is deficient in the exposed sights of the rock. The error is very large in these measurements. Therefore these results must be viewed with reservation.

The Th/U ratios, a weight ratio, have such a large amount of error that little can be said about their meaning.

The Ra^{226} in dpm compared to the U^{238}dpm also indicates heavy weathering. The Ra^{226}dpm is lower than that of the U^{238}.

The time extent of leaching follow the amount of U^{238} leached from the rock. Note the time vs. U^{238}dpm columns in Table III. The longer the rock was leached the more U^{238} was removed. The Ra^{226} decreased in amount on extended leaching which is expected since $RaCO_3$ is an insoluble substance.

In comparing the acid leaches of uranium and thorium it is noted that the uranium ratio U^{234}/U^{238} is generally lower than the thorium ratio Th^{228}/Th^{232}. This is reasonable since U^{234} is more likely to be deficient in the rock than Th^{228}. Th^{228} has a much shorter half life than does U^{234}. The Th^{228}/Th^{232} should remain closer to unity because of the short time for Th^{228} to grow into equilibrium with its parent Th^{232}.

The original assumptions were based on the assumption that U^{238} and Th^{232} would be in equilibrium with their daughter products. Since this was found not to be the case especially with uranium judgements must be made with this in mind.

It is the opinion of the author that the major cause of high ratios by weak leaches is due primarily to the effect of alpha decay on the position of the daughter products in the crystal lattice. A model was set up to explain the data. Further work will be necessary to prove or disprove the validity of this model. The author suggests several prospects for future work. These included the following. The leach of Storm King Granite with very weak acid solutions. It is hoped that such leaches might show a preference for U^{234} compared to U^{238} perhaps giving ratios greater than one. Weak carbonate solutions might also be tried. In order to test the validity of the model the different mineral parts of Storm King Granite might be separated and their uranium and thorium ratios measured. A nitric acid leach might be tried to see the effects of the nitrate ion and its possible oxidizing effects. More leaching might be done with weak HCl and H_2SO_4 leach in order to study the effects of the anions Cl^- and $SO_4^=$. Leaches with humic acid might also be attempted since its effect in nature may be of importance.

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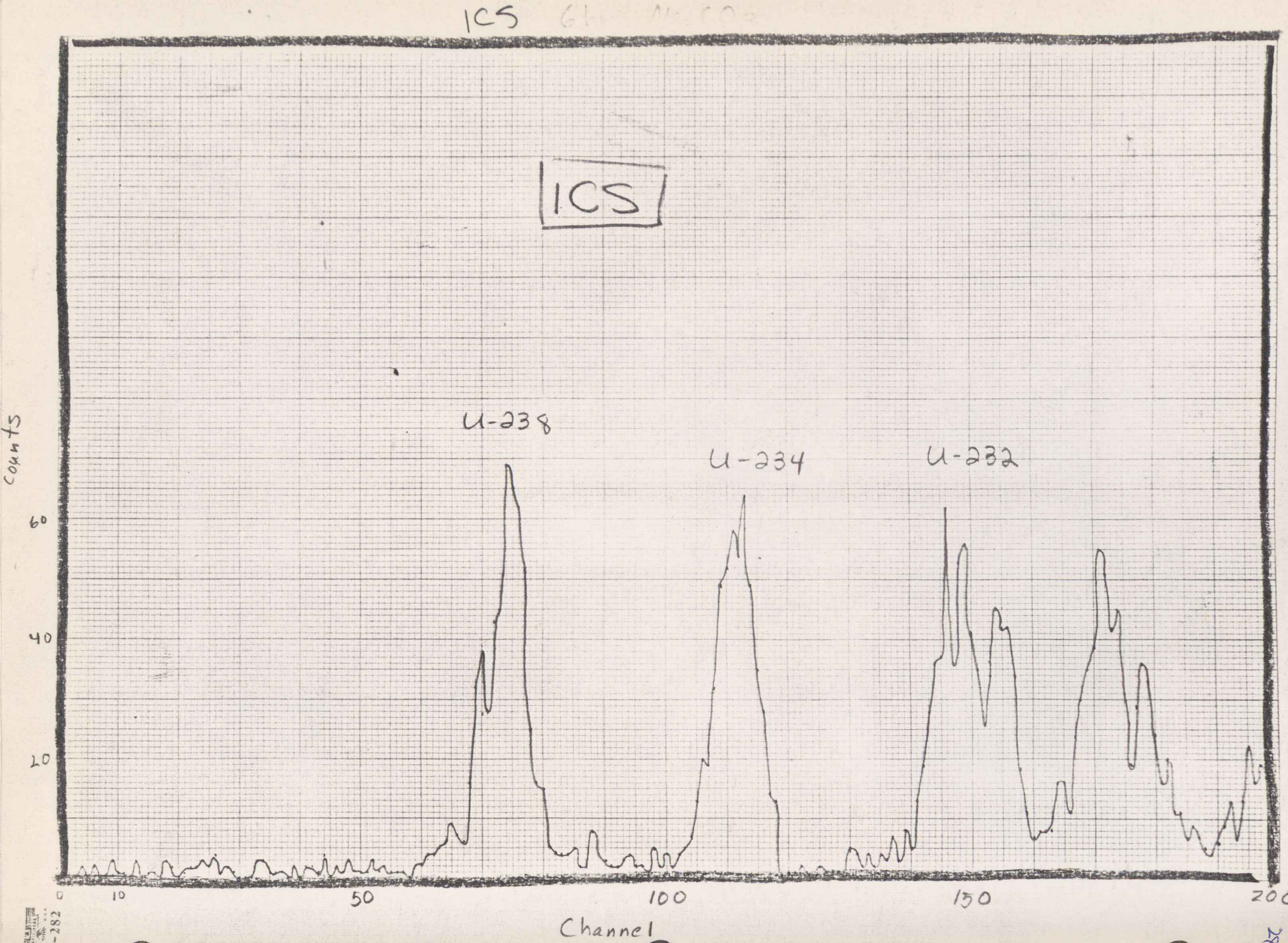
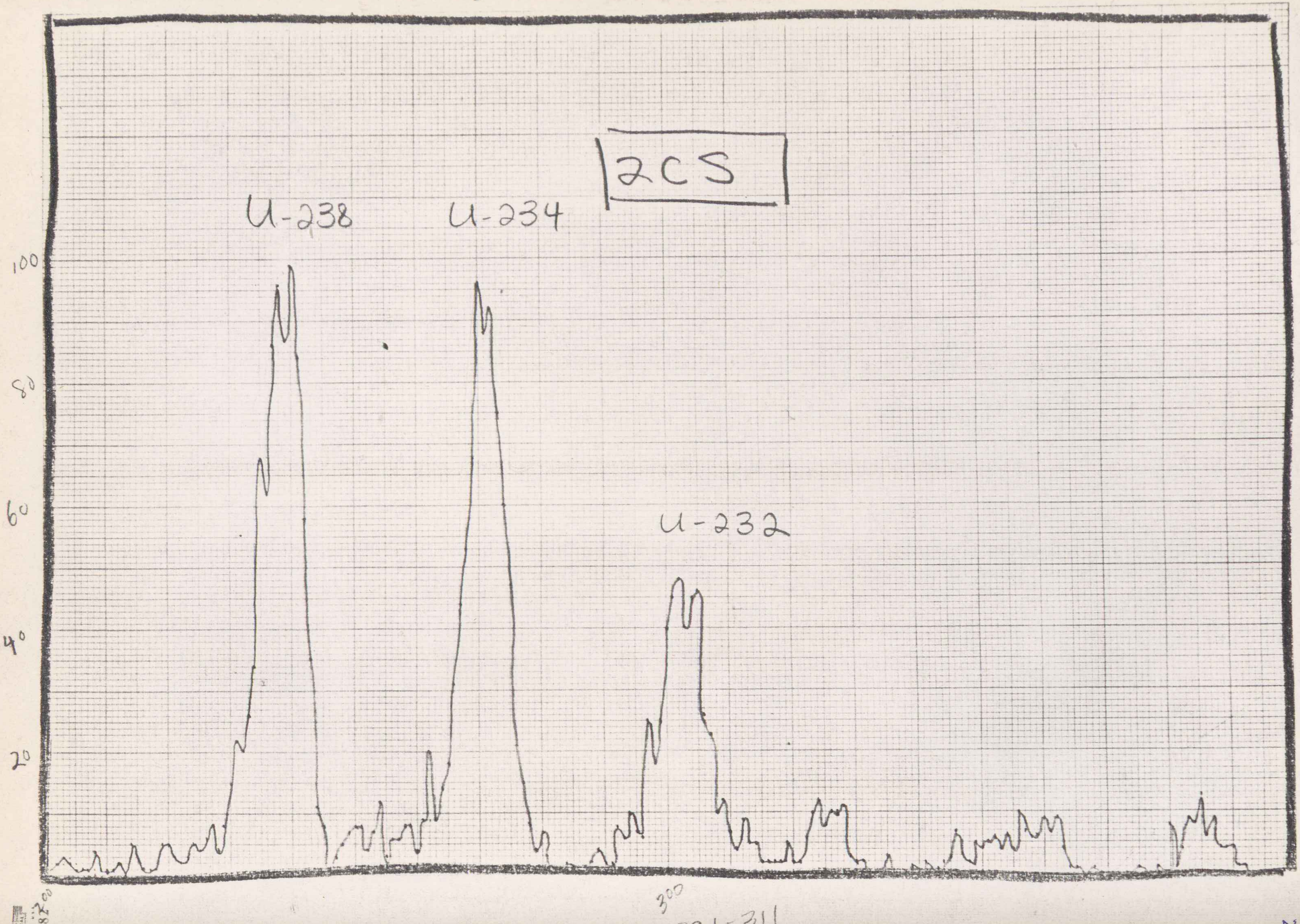
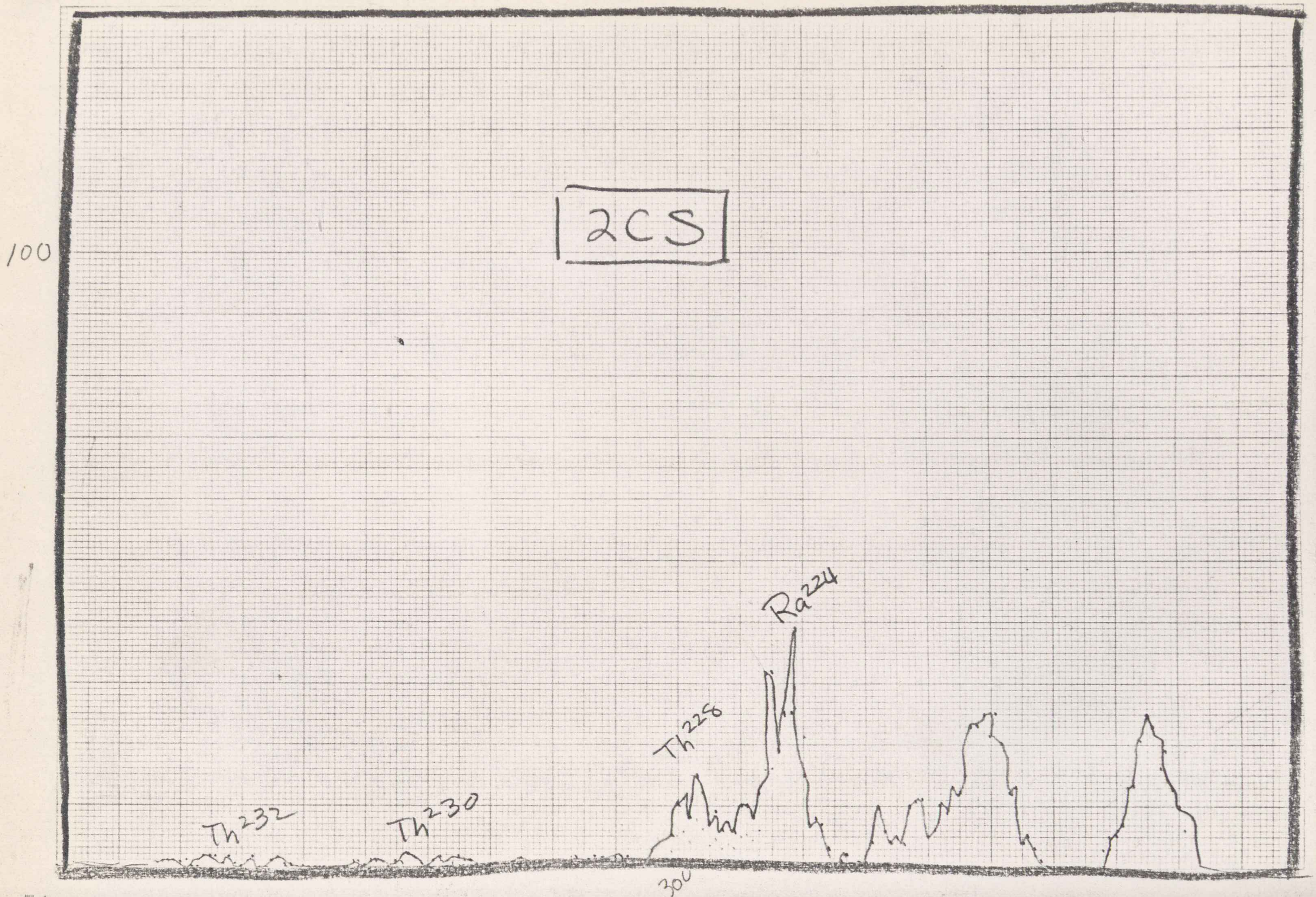


Squares to the Inch

2CS



2CS Th



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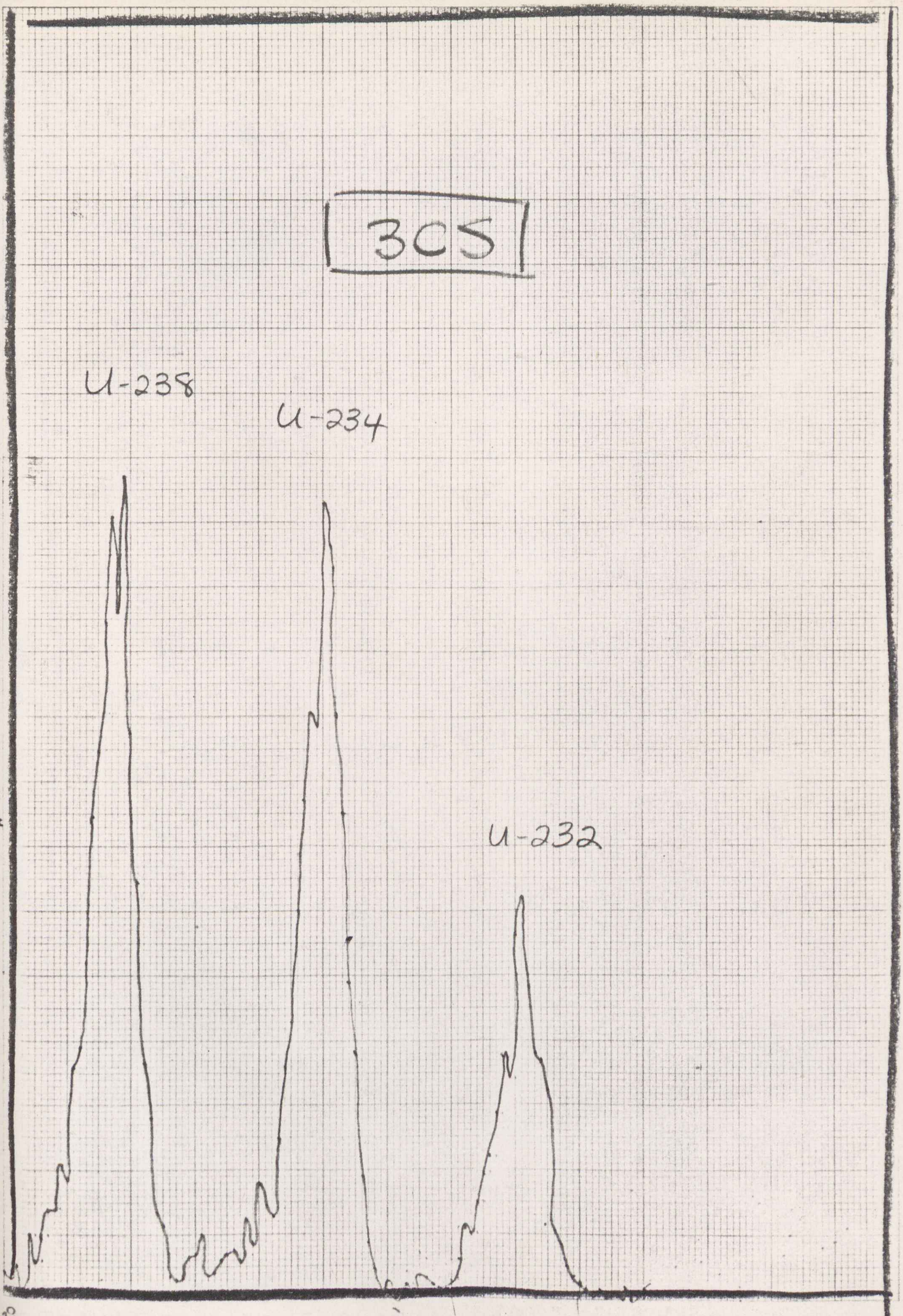

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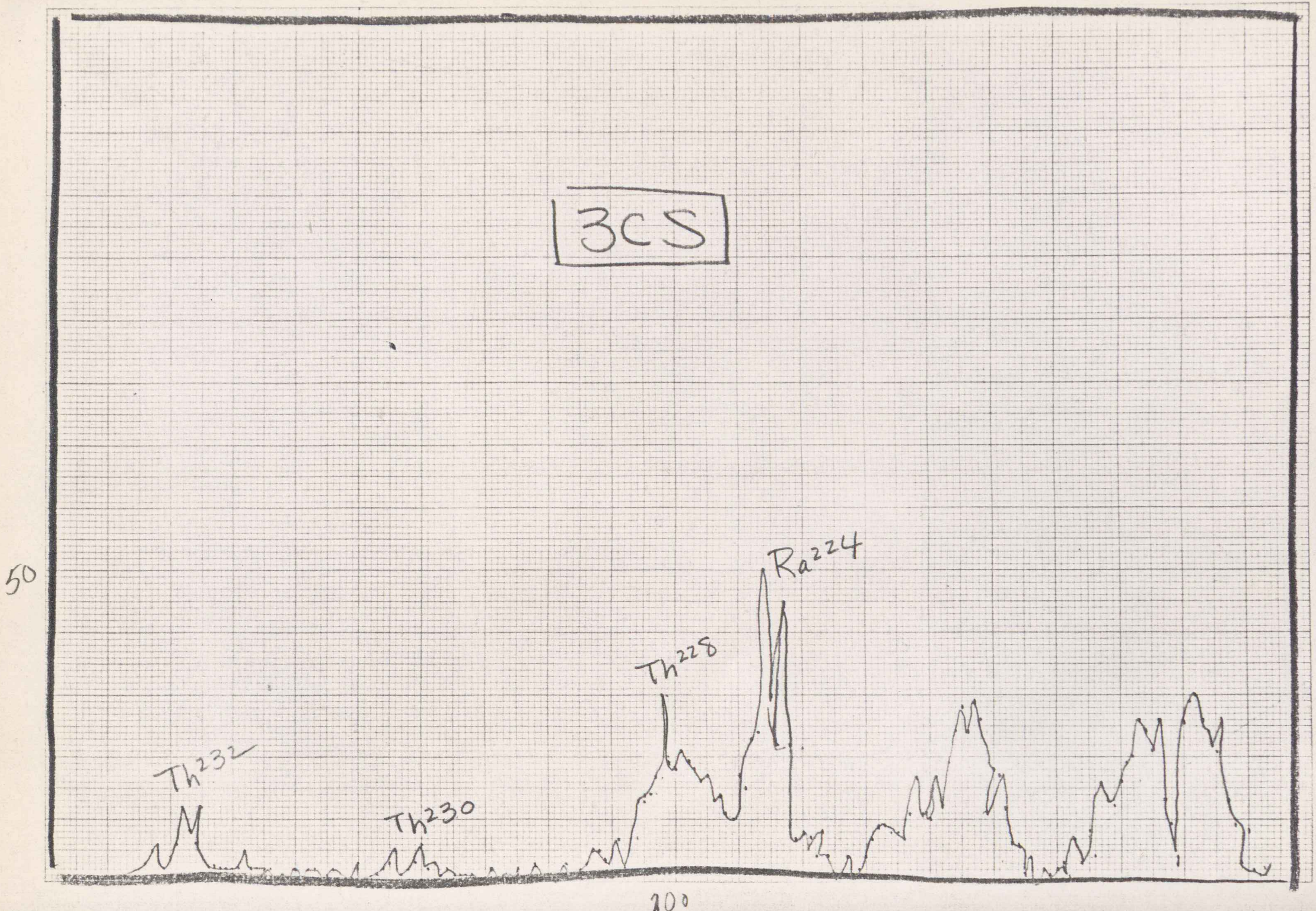
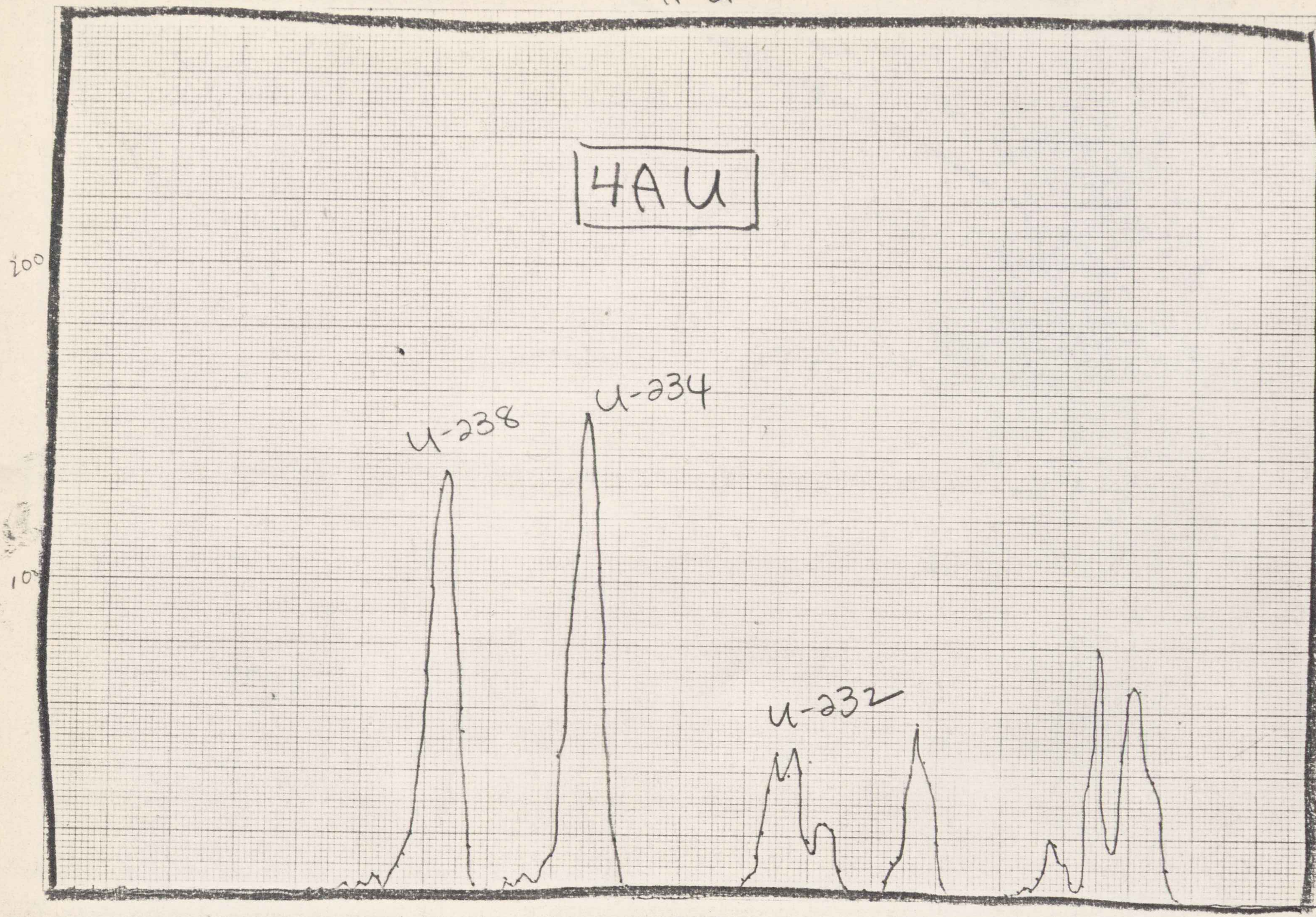


4A U



282

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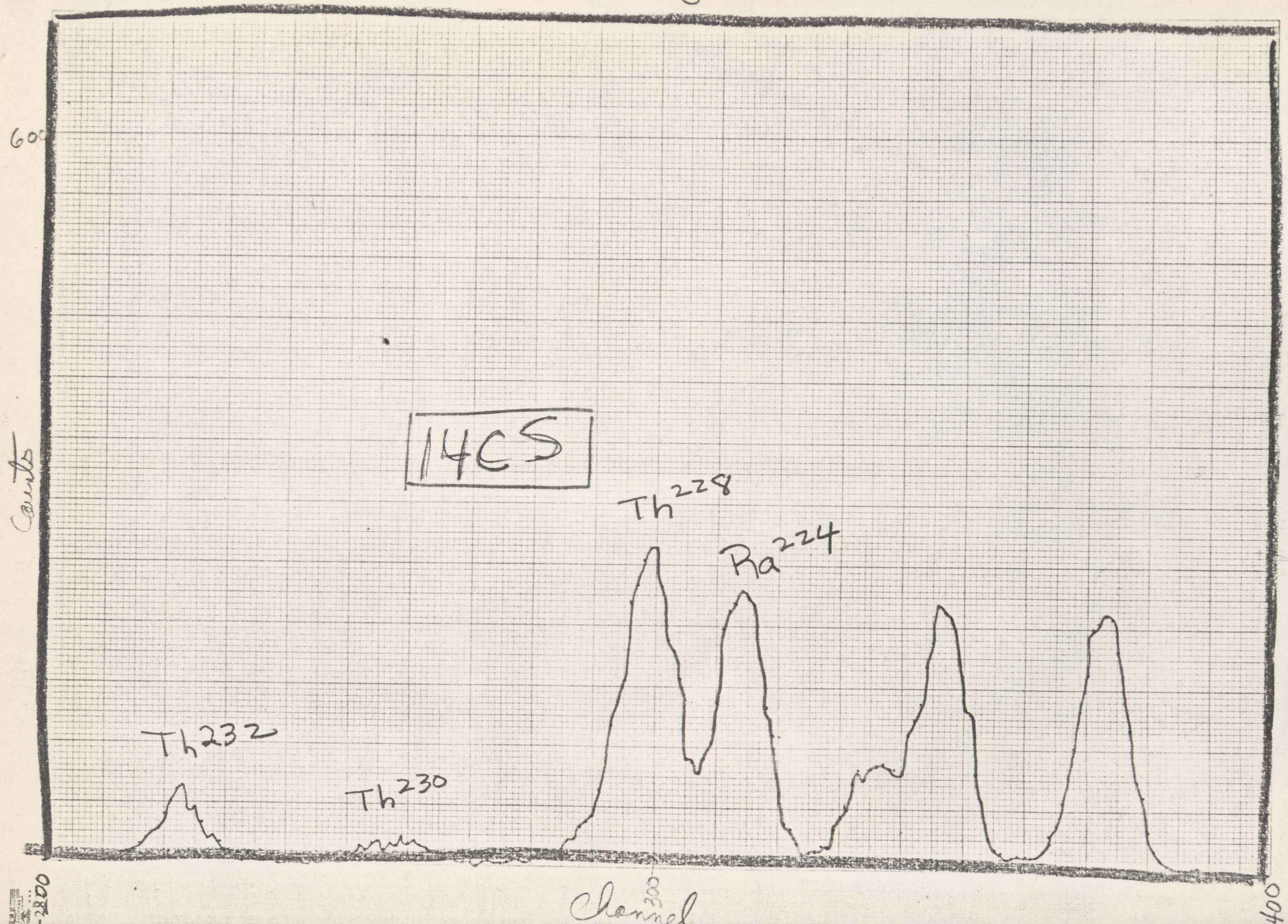
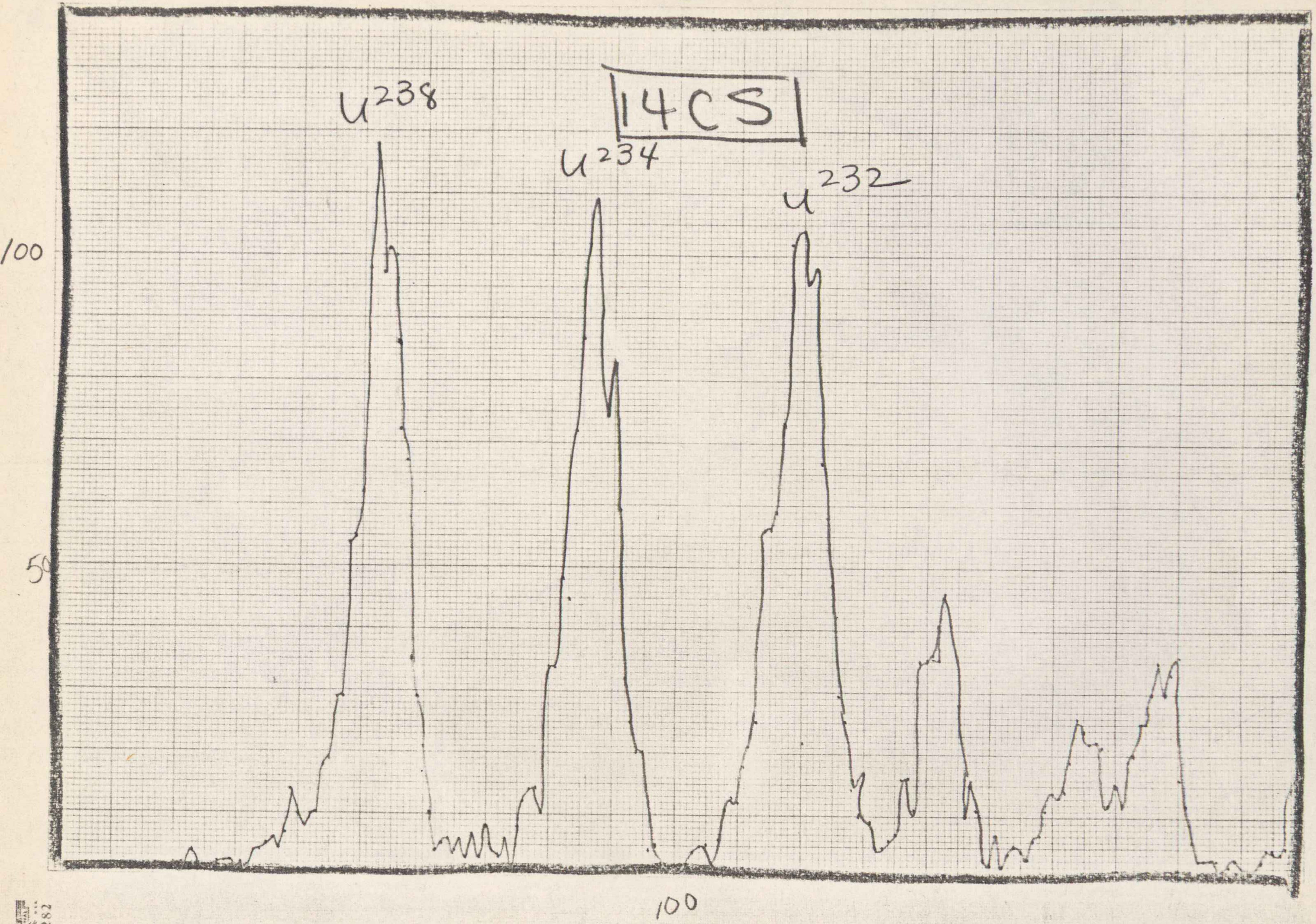
14CS



squares to the Inch

14CS



-282

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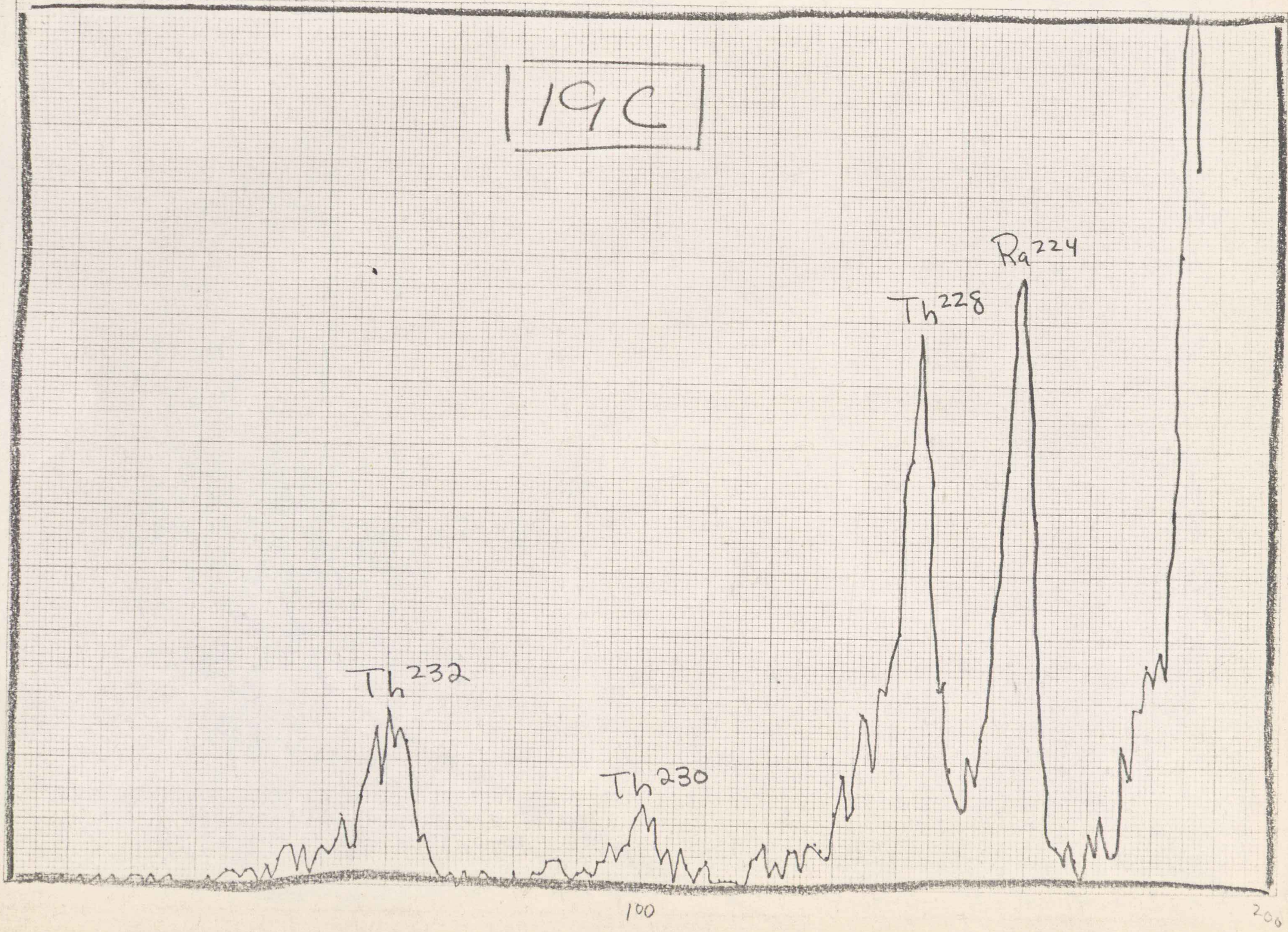
19C



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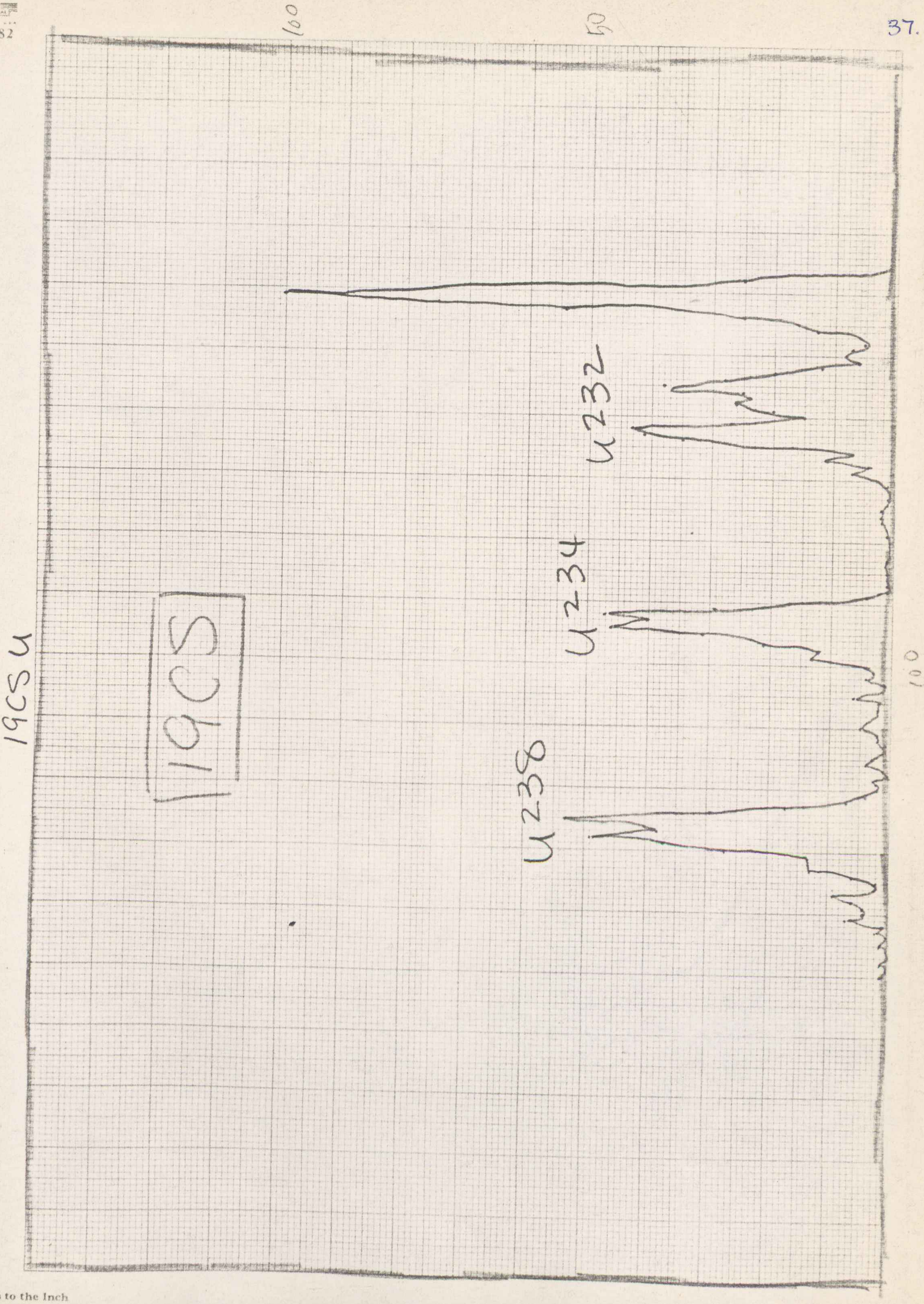

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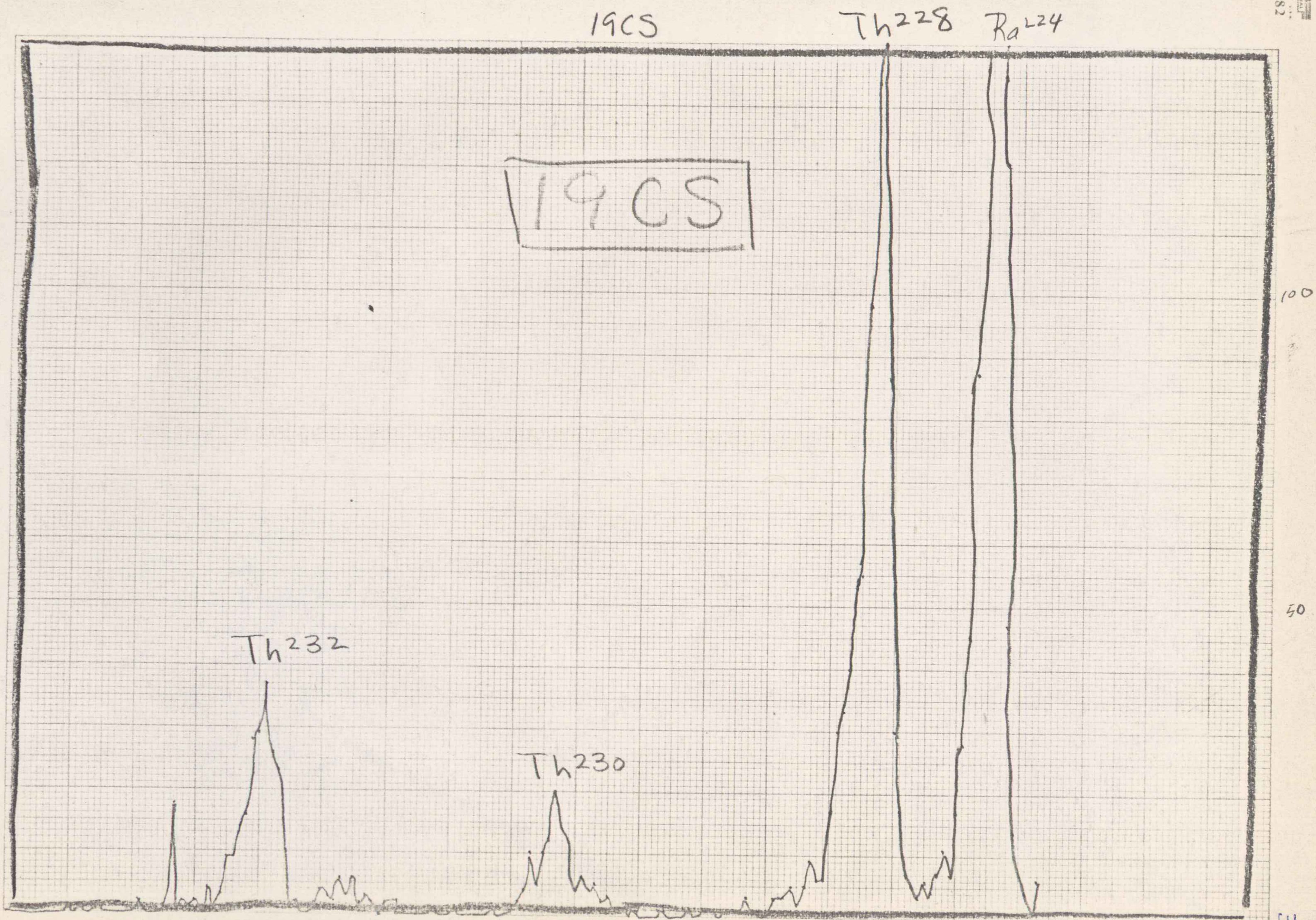
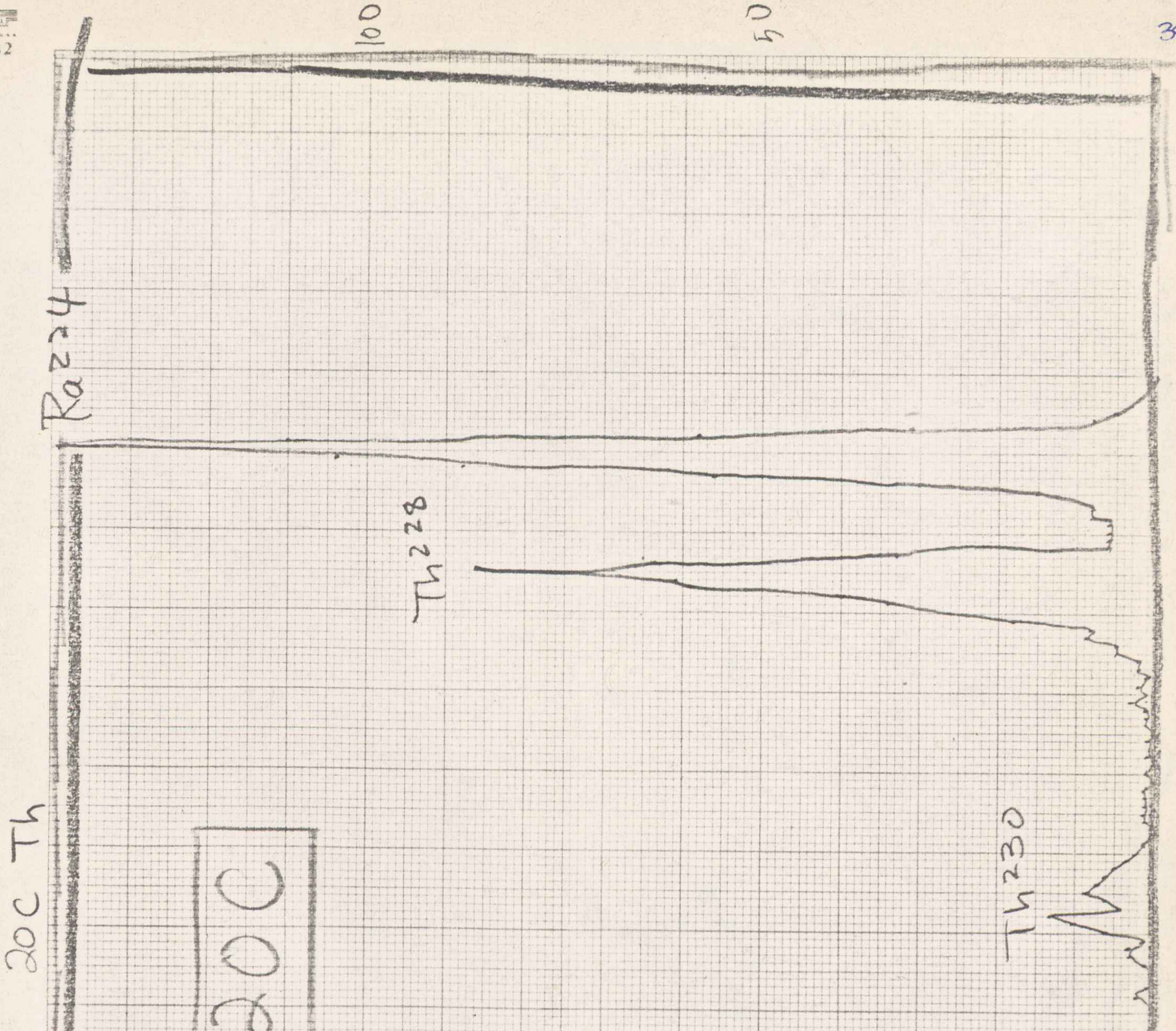
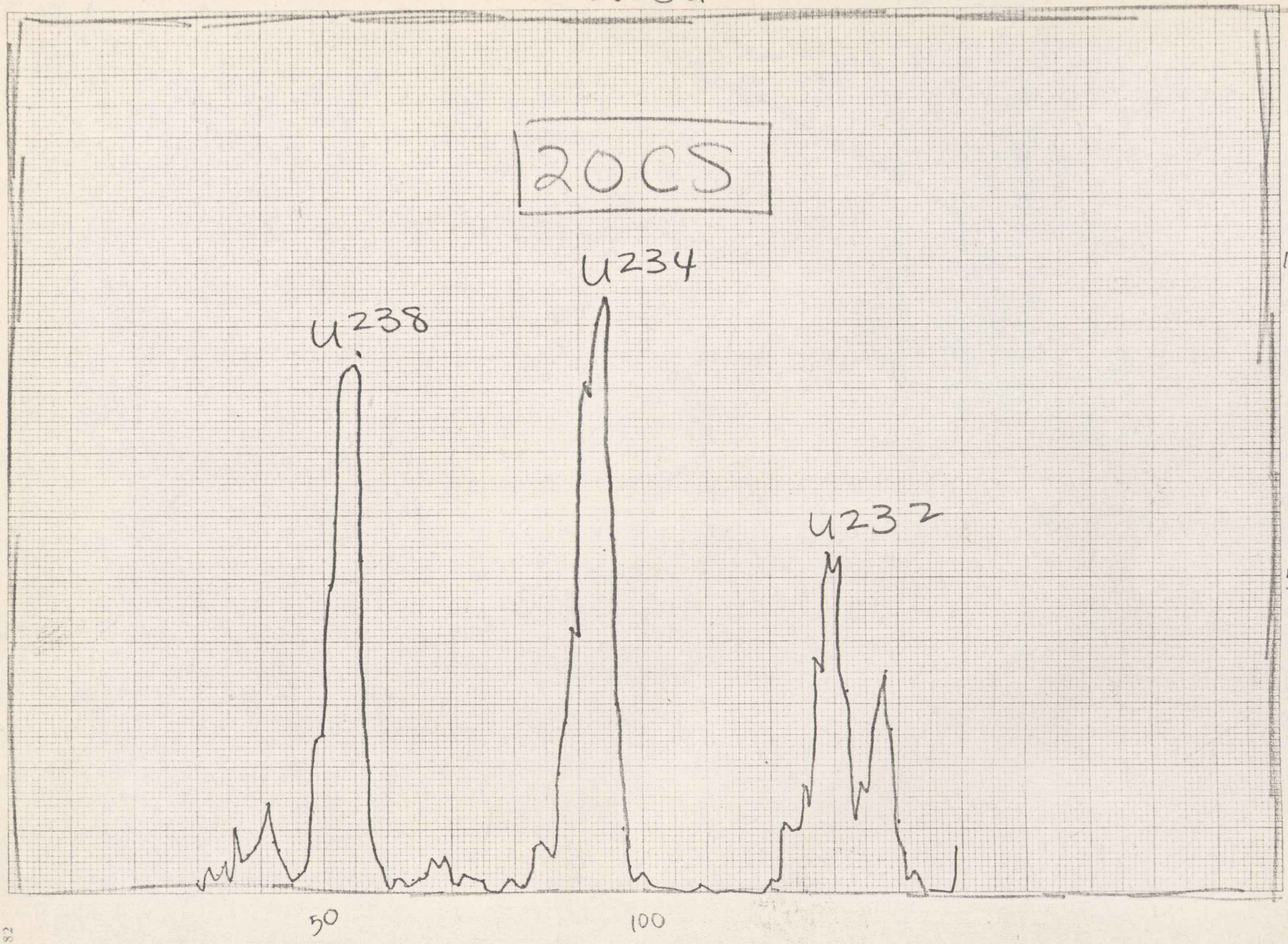

19CS
Th228
Ra224
19CS
100
50
Th232
Th230

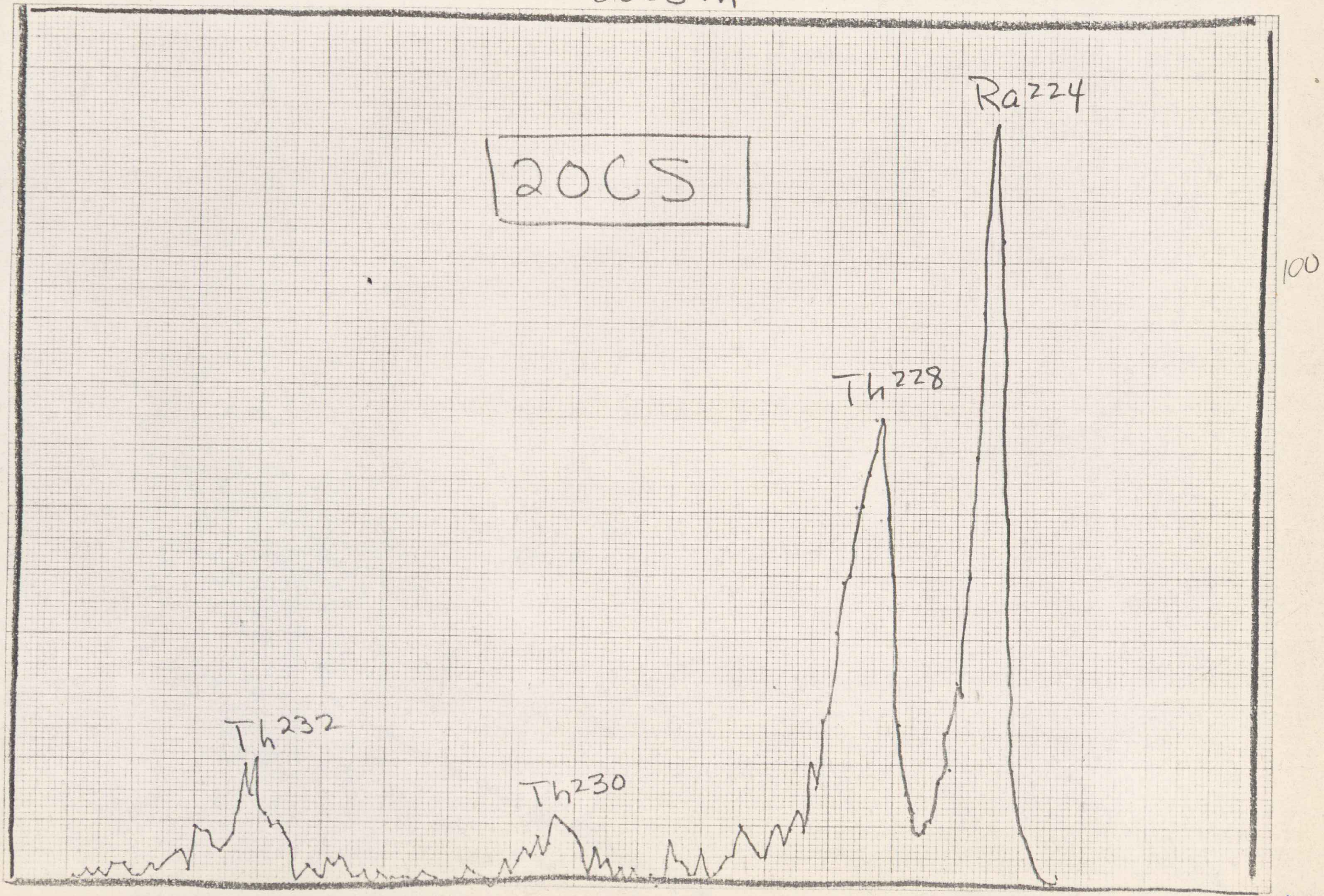

100
50
Ra224
Th228
20c Th
20C
Th230
Th232

20CS4

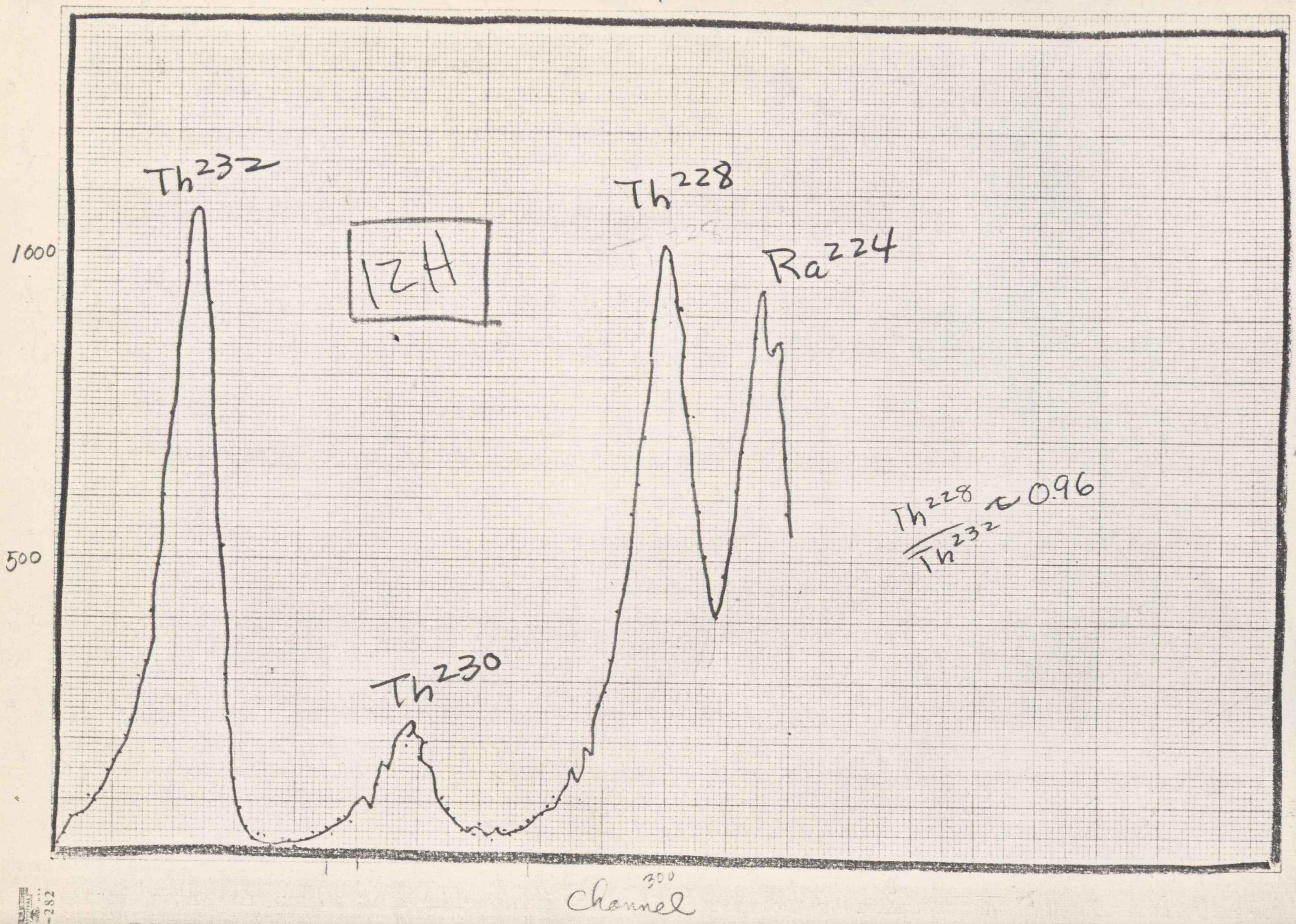


Squares to the Inch

20CSTh

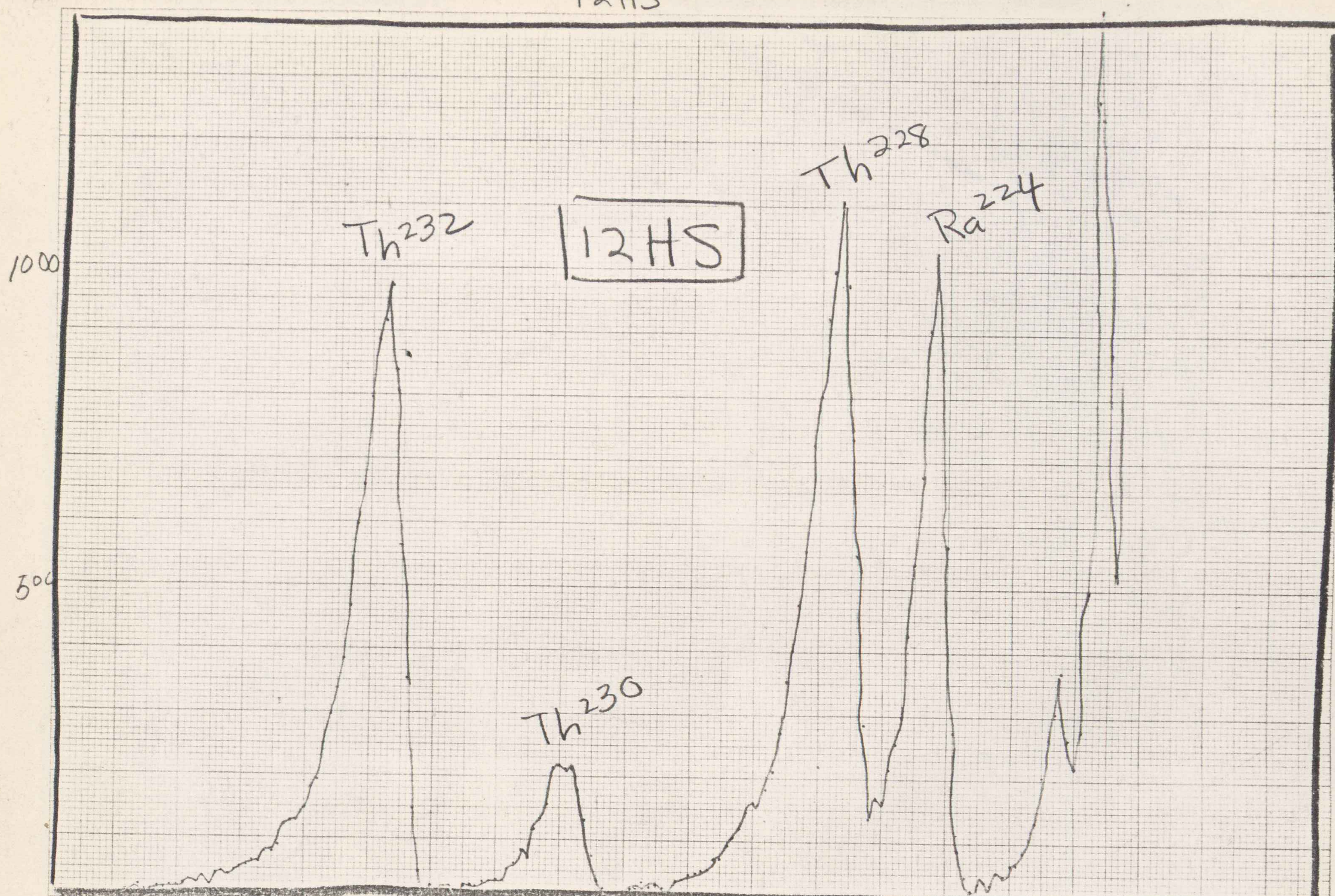


12H

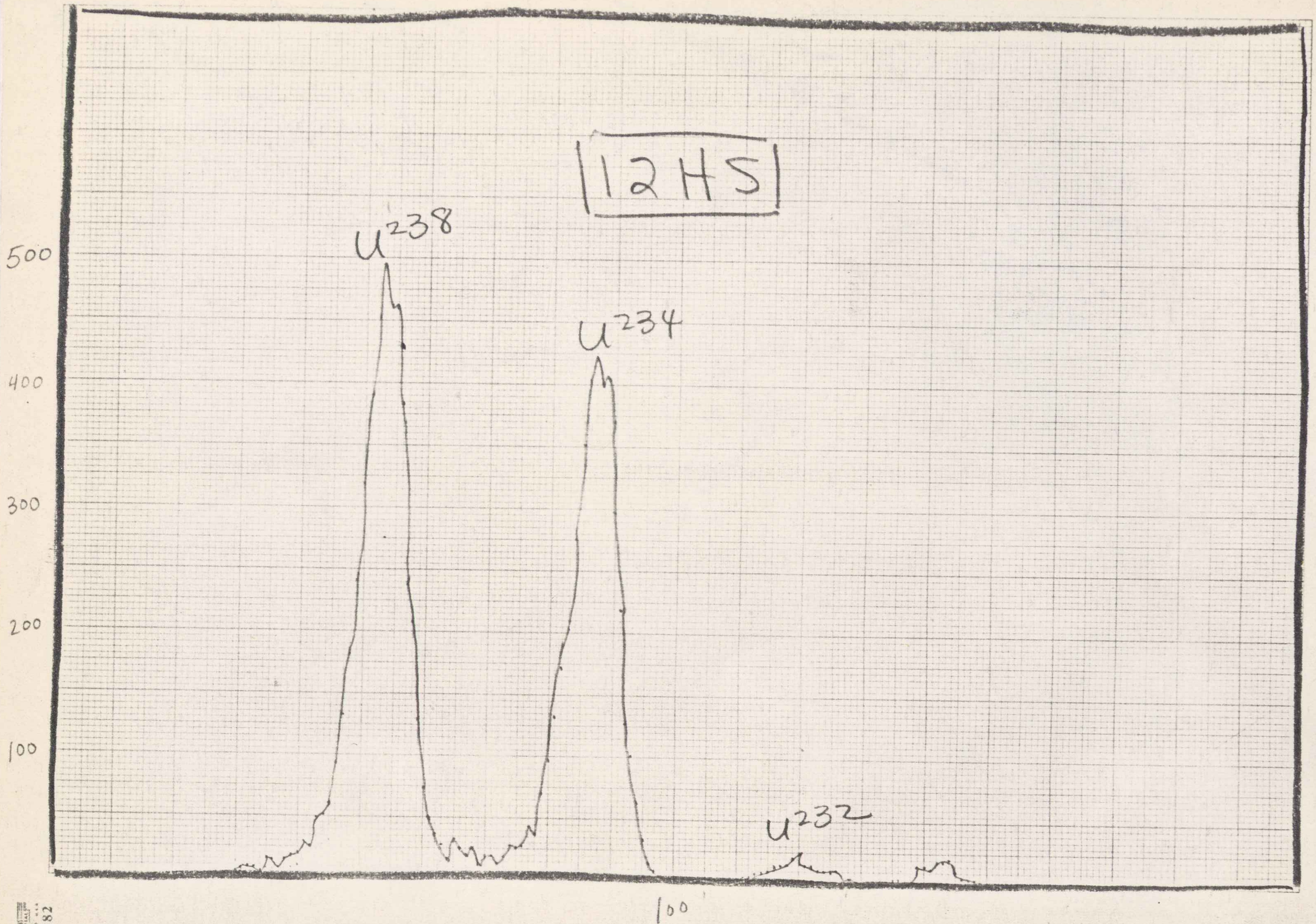


12H
Th^{232}
Th^{230}
Th^{228}
Ra^{224}
$\frac{Th^{228}}{Th^{232}} \approx 0.96$
1000
500
300
Channel

12HS



12HS



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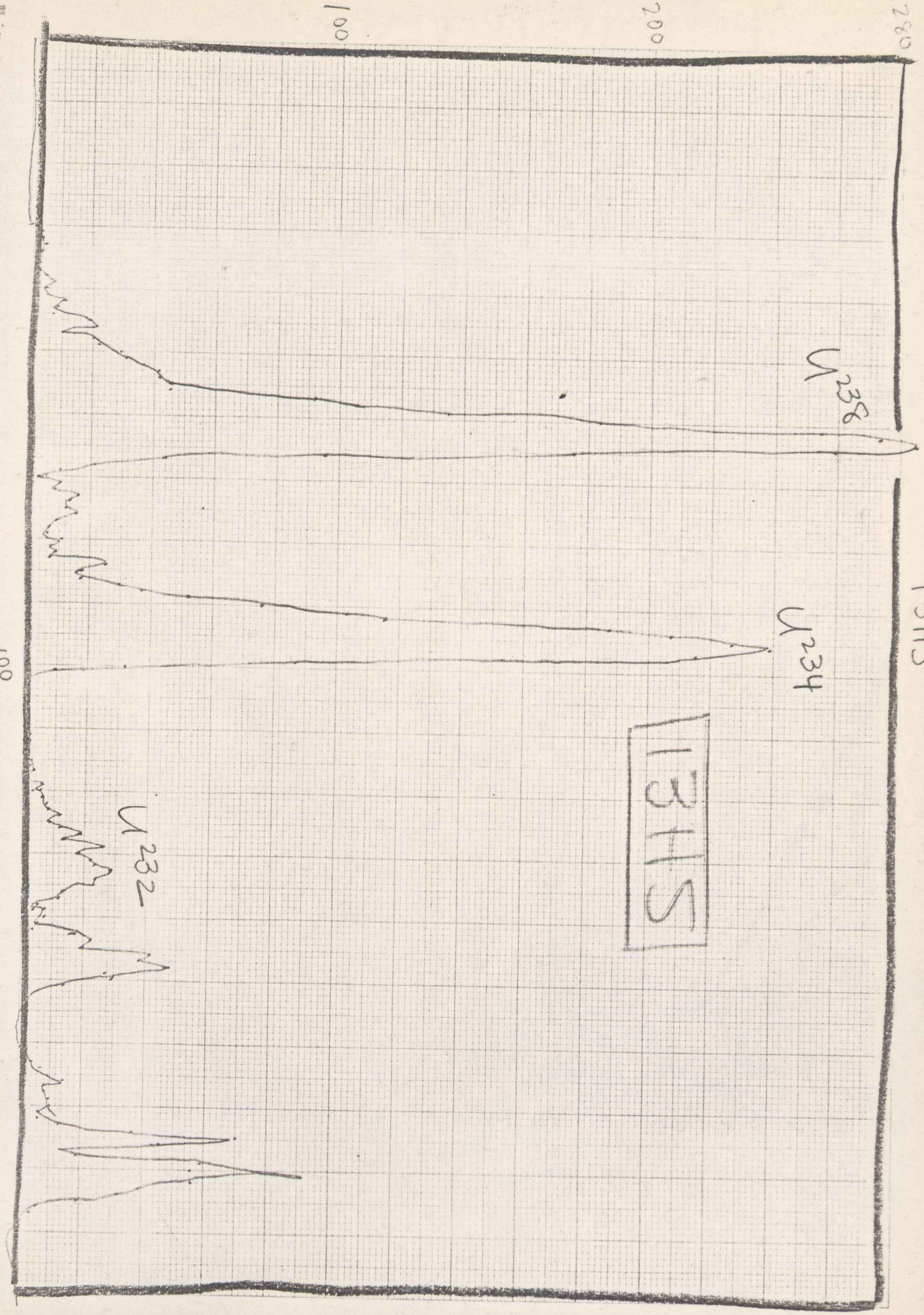
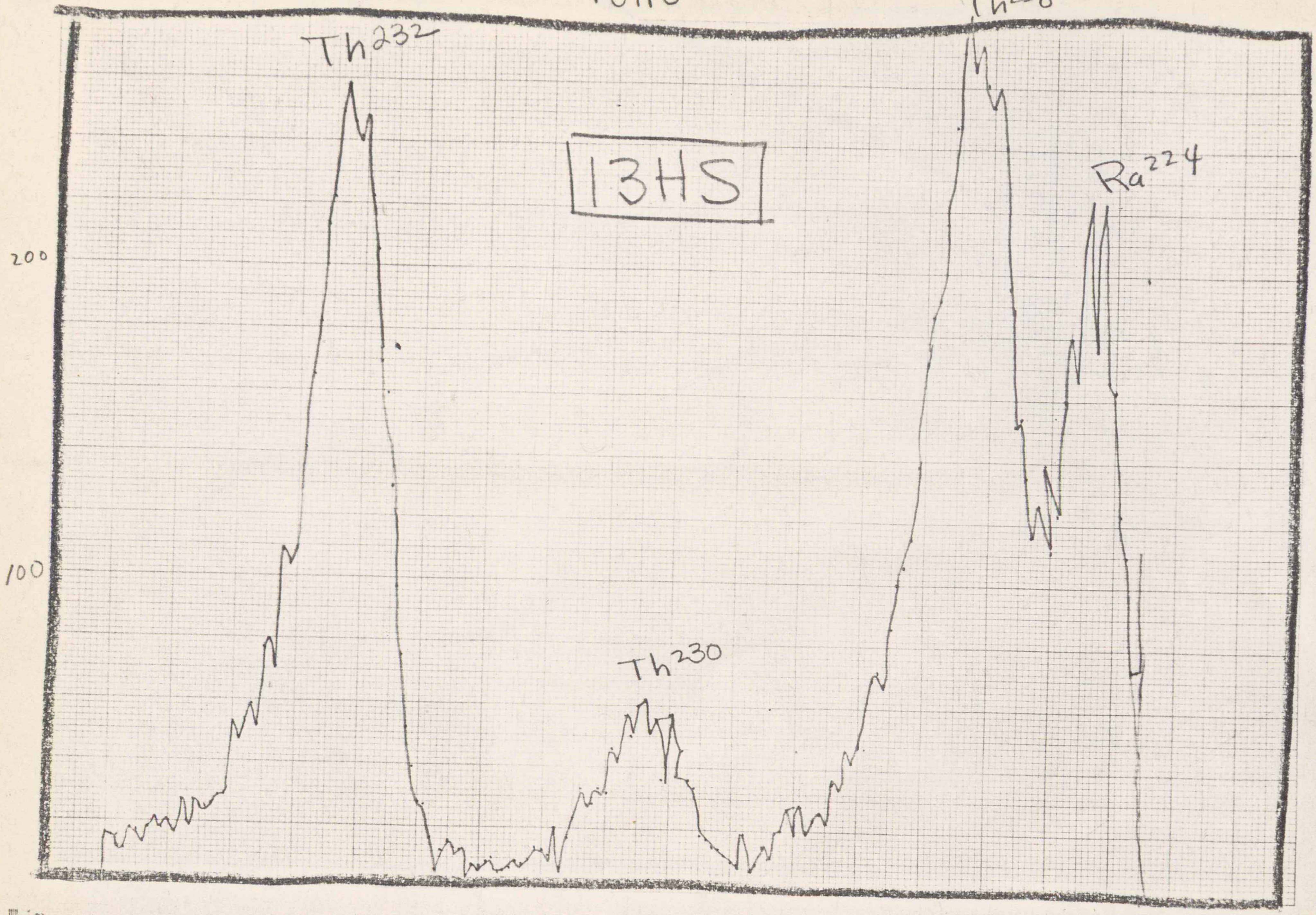


ares to the Inch

13HS



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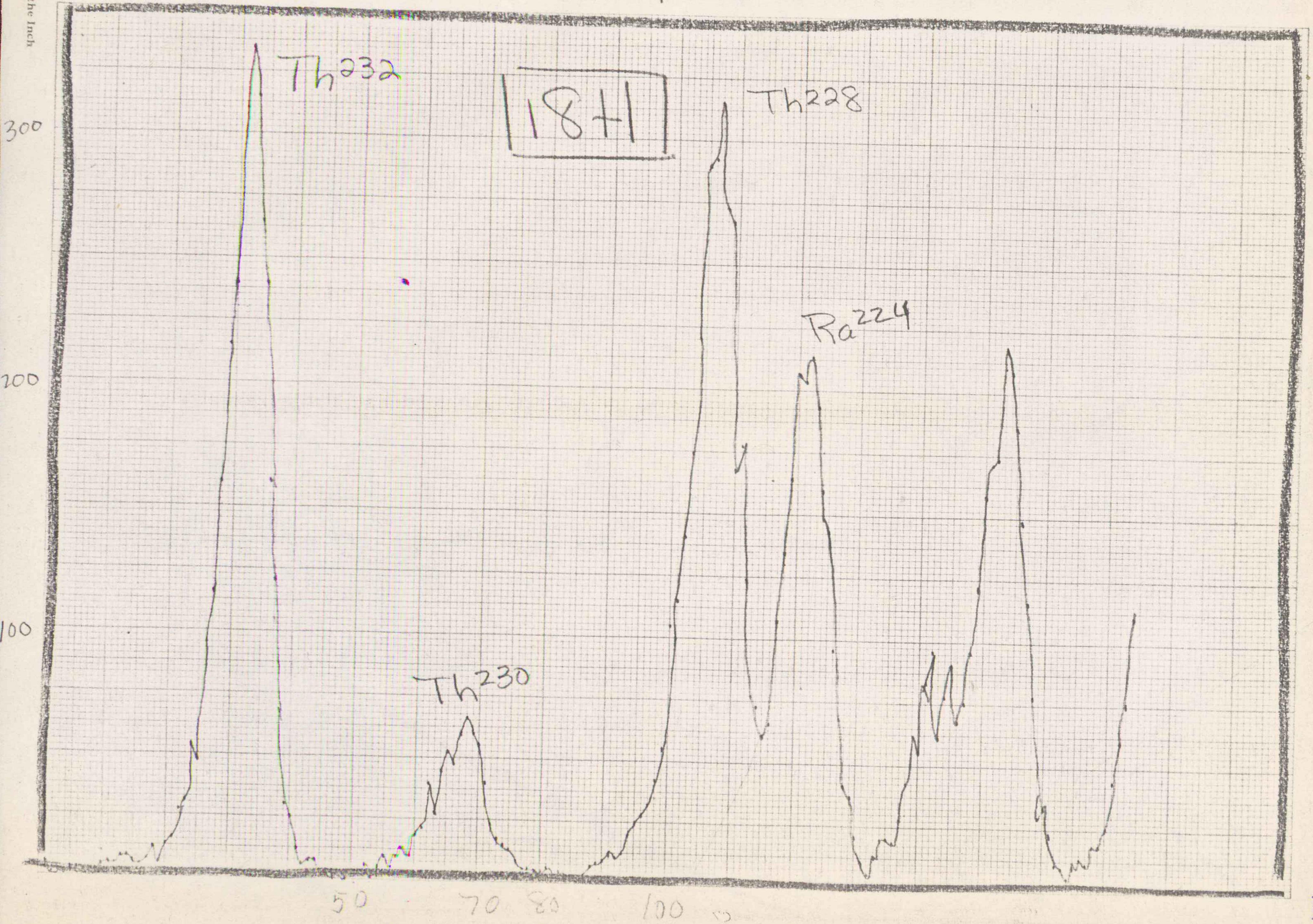
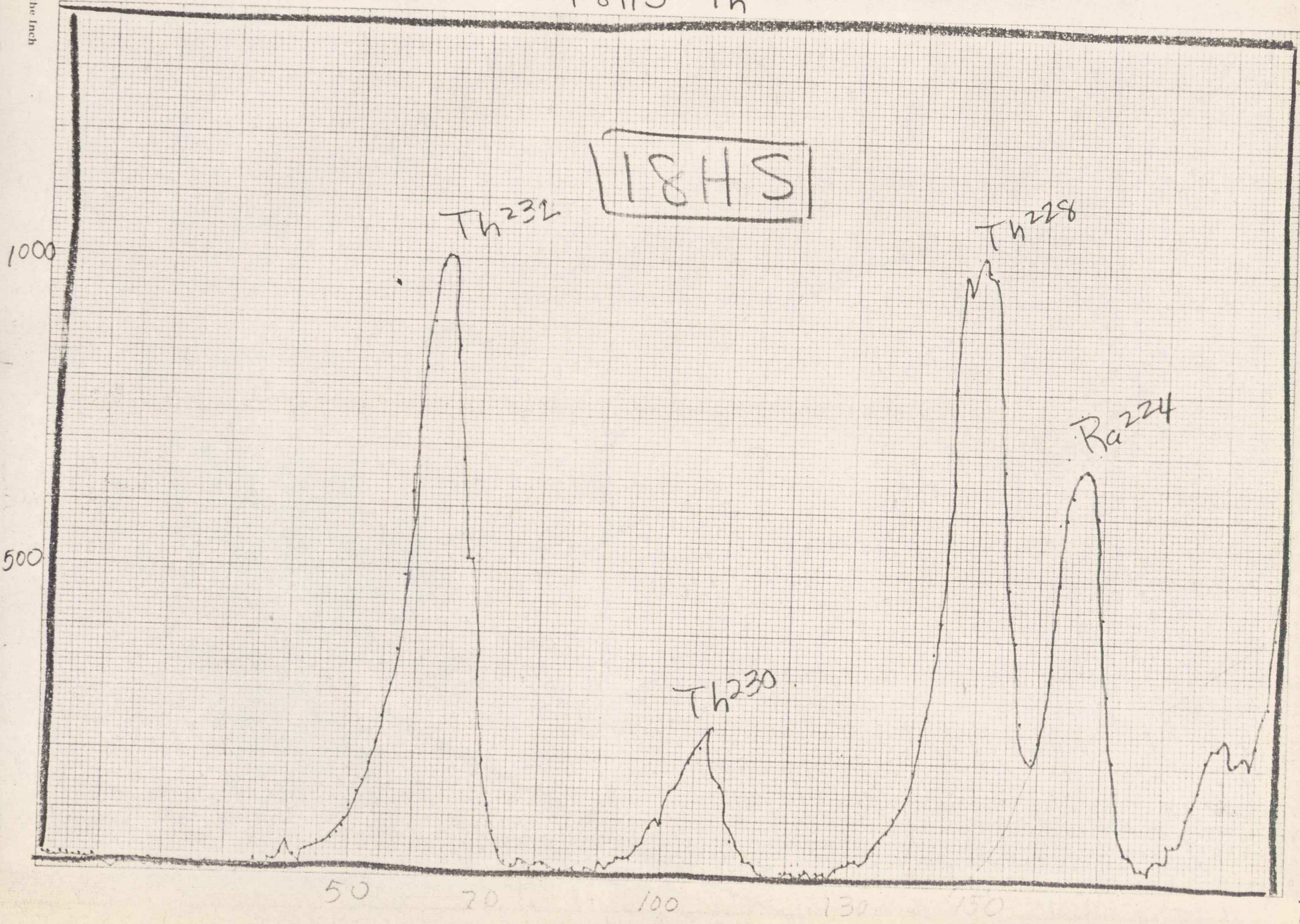
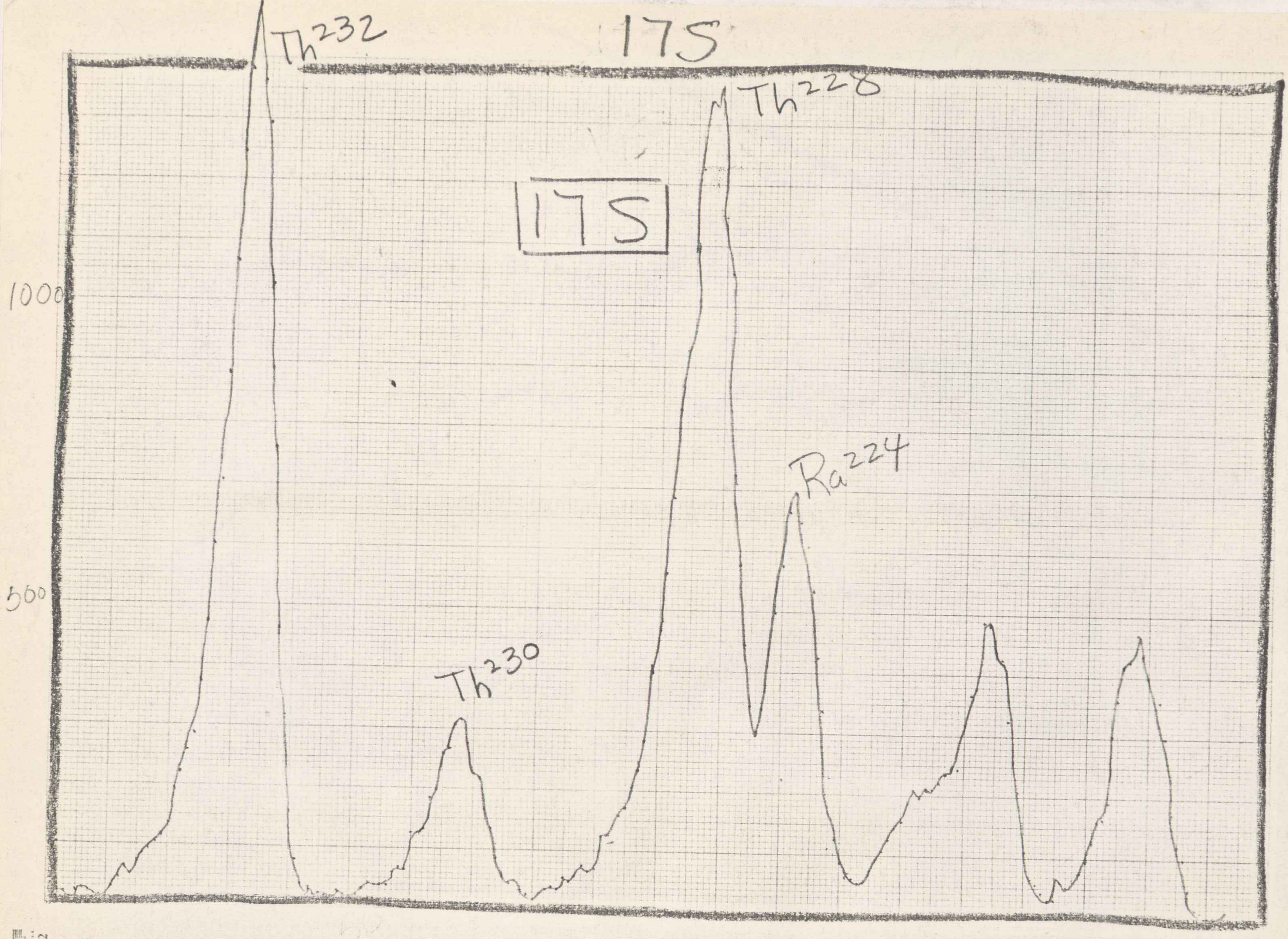
18H Th

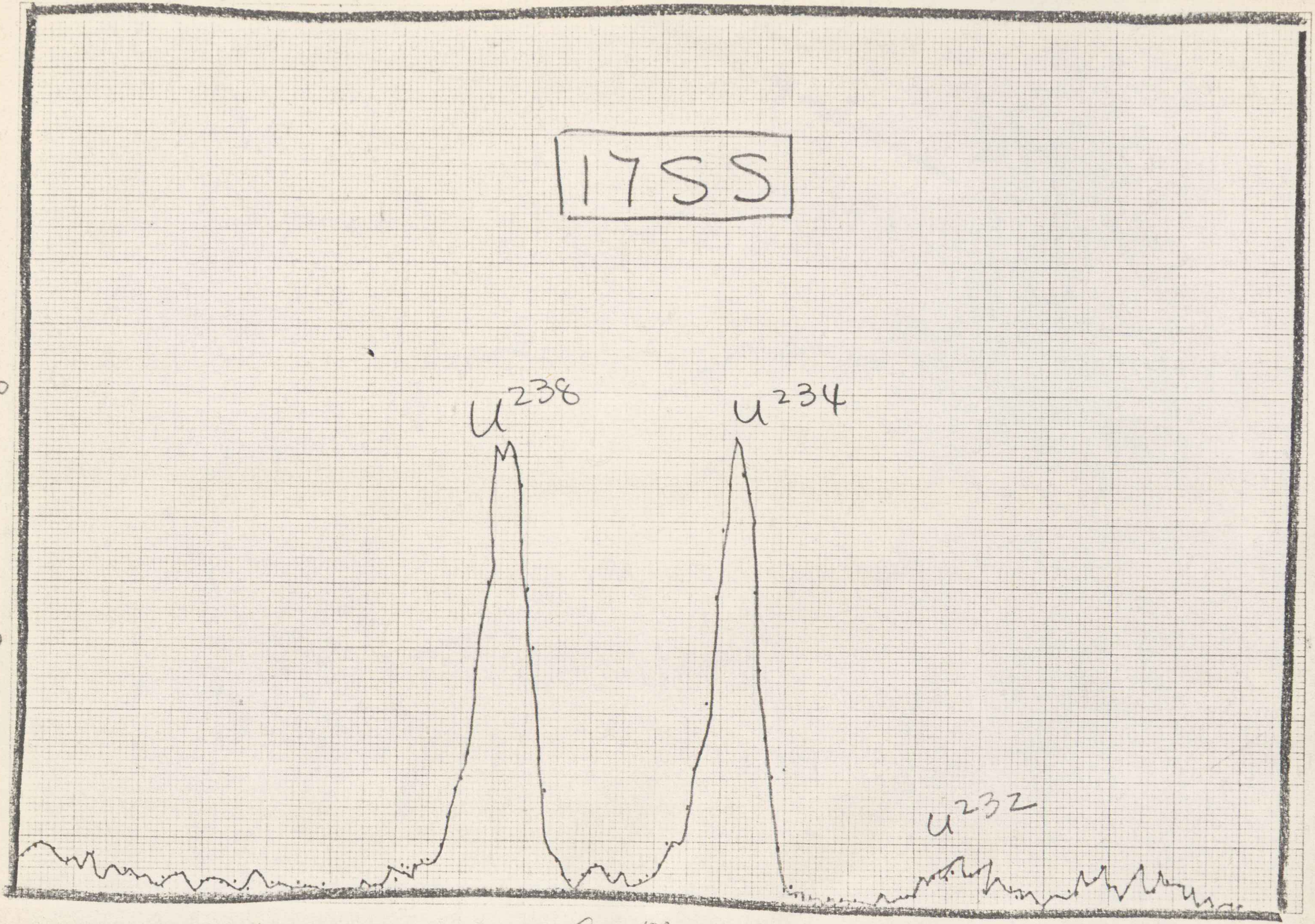


18HS Th




175
Th232
175
Th228
1000
Ra224
500
Th230

17SS



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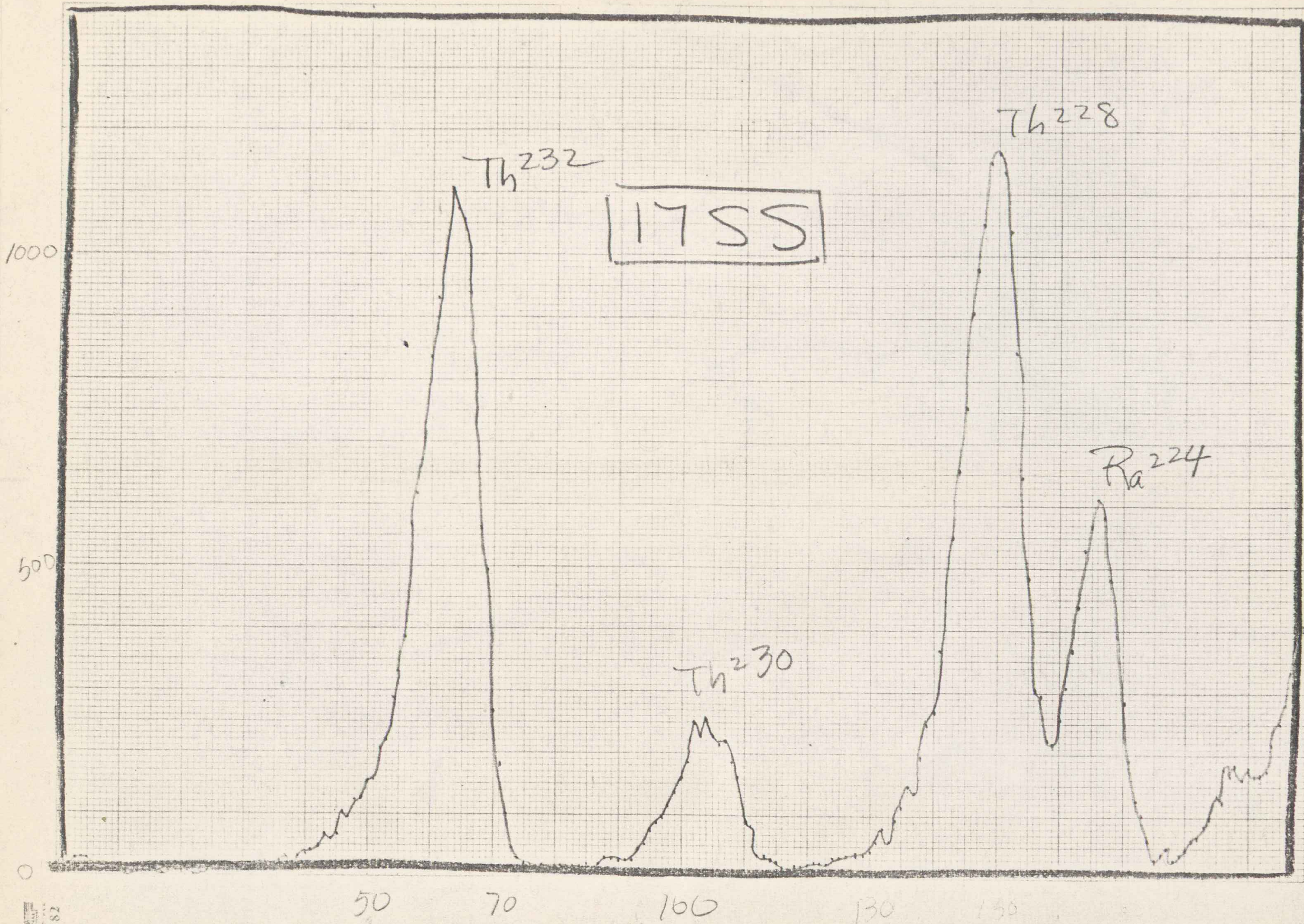
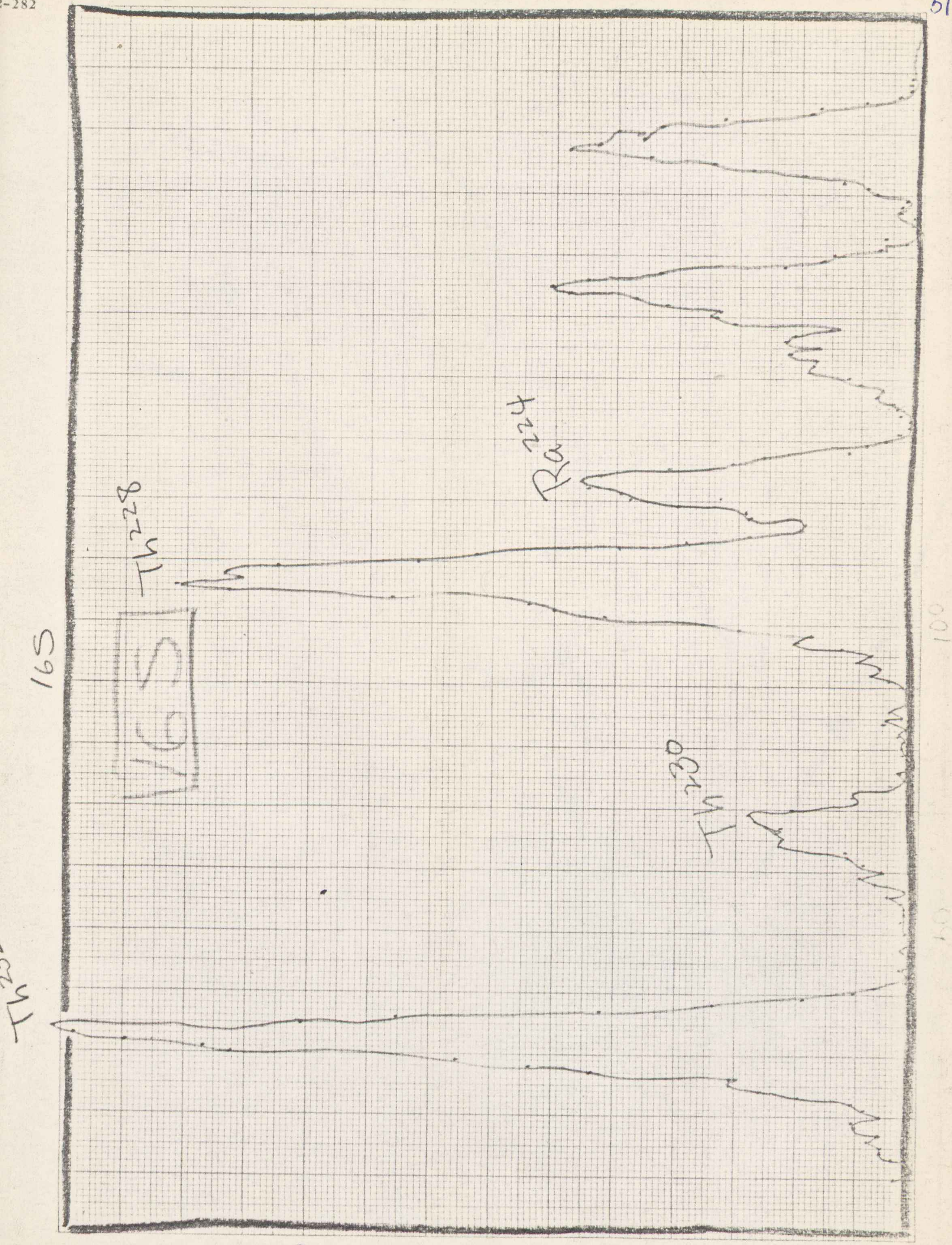
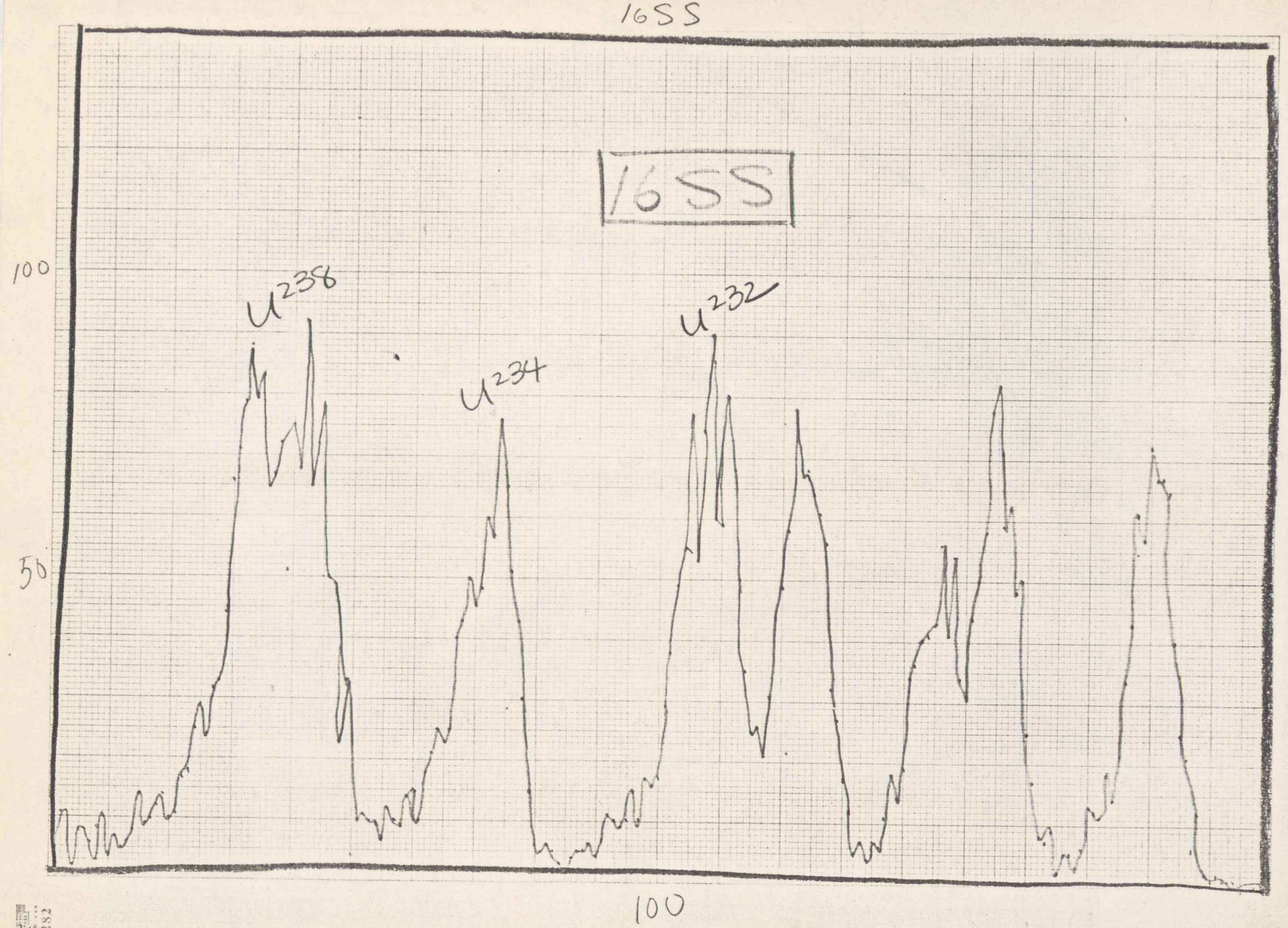



Th228
Ra224
Th230
165
165
200
160
100



uares to the Inch

16SS