Mr. H. W. Smith

Industrial Confidential

DECLASSIFIED
DATE Nov 22 1978
AUTHORIZED BY

CANADA

DEPARTMENT OF MINES AND TECHNICAL SURVEYS

OTTAWA

MINES BRANCH INVESTIGATION REPORT IR 60-50

SEARCH FOR PROTACTINIUM -231 IN URANIUM LEACH LIQUORS

by

G. G. EICHHOLZ AND C. McMAHON

MINERAL SCIENCES DIVISION

NOTE: THIS REPORT RELATES ESSENTIALLY TO THE SAMPLES AS RECEIVED. THE REPORT AND ANY CORRESPONDENCE CONNECTED THEREWITH SHALL NOT BE USED IN FULL OR IN PART AS PUBLICITY OR ADVERTISING MATTER.

COPY NO. 14

MAY 6, 1960

Mines Branch Investigation Report IR 60-50

SEARCH FOR PROTACTINIUM-231 IN URANIUM LEACH LIQUORS

by

G.G. Eichholz[*] and C. McMahon[**]

- - -

SUMMARY OF RESULTS

Five uranium solution samples obtained from leach products of the Port Radium and Port Hope plants of Eldorado Mining and Refining Limited were investigated on an alpha-ray spectrometer to establish the possible presence of protactinium-231, a daughter product of uranium-235, in measurable quantities. Only one of the samples, which was prepared from a concentrate of Port Hope raffinate, showed evidence of the presence of Pa-231. A description is presented of all the alpha-ray spectra obtained.

---

[*] Head and [**] Senior Technician, Physics and Radiotracer Section, Mineral Sciences Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

INTRODUCTION

In February 1960 a request was submitted to the Physics and Radiotracer Section by Mr. E.B. Spice of Eldorado Mining and Refining Limited to determine the possible presence of protactinium-231 in various by-products of uranium extraction processes by means of alpha-ray spectrometry. The interest in Pa-231 arose from the fact that it is an alpha emitter of half-life 34,300 years, with a specific activity of 1.014×10^5 dpm/μg. Its alpha-particle energies in MeV obtained by spectrographic measurements (1) are: 5.046 (10%), 5.017 (23%), 5.001 (24%), 4.971 (2.3%), 4.938 (22%), 4.921 (2.8%), 4.839 (1.4%), 4.722 (11%), 4.696 (1.4%), 4.666 (2.1%), or in round terms about 84% at 5.0 MeV and about 14.5% at 4.7 MeV. It also emits some low-energy gamma radiation. These properties make Pa-231 potentially valuable foruse in neutron sources, if it can be extracted economically.

In order to distinguish protactinium-231 unambiguously from all other alpha emitters present in uranium leach liquors it must be clearly resolved from the other alpha-particle energy peaks. Table 1 lists the alpha-particle energies of all these alpha emitters.

TABLE 1

Alpha-particle Energies (in MeV)

	Uranium Series		Neptunium Series		
isotope	α-energy	half-life	isotope	α-energy	half-life
U-238	4.18	4.6×10^{9} yr	U-235	4.36, 4.56	7.1×10^{8} yr
U-234	4.768	2.7×10^{5} yr	Pa-231	5.0 , 4.7	3.43×10^{4} yr
Th-230	4.68	8.3×10^{4} yr	Th-227	6.0 , 5.72	18.2 d
Ra-226	4.78	1622 yr	Ra-223	5.71, 5.60	11.7 d
Rn-222	5.48	3.83 d	Rn-219	6.81, 6.55	3.9 sec
Po-218	6.00	3 min	Po-215	7.36	1.8 msec
Po-214	7.68	164 μsec	At-215	8.00	100 μsec
Po-210	5.30	140 d	Bi-211	6.22, 6.27	2.16 min
			Po-211	7.44	25 sec

At equilibrium each daughter element will be present in an abundance ratio to its longest-lived parent proportional to their half-lives. The normal abundance of U-235 is 0.7% of the U-238 content of the source material. It follows also that any very short-lived isotope (half-life less than one week) will decay away rapidly once it has been separated from its parent element.

Since U-235 and U-238 will not be separated by any purely chemical processes, all uranium ores contain a certain amount of Pa-231, 0.35 µg/g U. This protactinium may be separated from the uranium in the course of extraction and refining. However, because of the very small amount present, determination by chemical means is difficult and a radiometric method is preferred. For good resolution on an alpha-ray spectrometer, it is important to prepare thin sources of as high a concentration as possible, and this step constitutes the main stumbling block in obtaining quantitative and reproducible assay values.

The alpha-ray spectrometer used is one patterned on the Chalk River equipment described by Harvey et al.(2). It consists of a large gridded ionization chamber, operated with a argon-methane filling, with a built-in preamplifier, a type AEP-1444 low-noise amplifier unit, and a Marconi six-channel kicksorter (3). Because of the low activity of the samples long runs had to be taken. The spectrometer was calibrated by means of a polonium source (5.30 MeV) and a pure uranium source (4.18 and 4.76 MeV).

SAMPLE PREPARATION

Five samples were submitted:

Sample 1 - Concentrate from Port Radium raffinate

Sample 2 - Concentrate from Port Hope raffinate

Sample 3 - Concentrate from Port Radium concentrate

Sample 4 - Concentrate from Port Hope UO_3

Sample 5 - Concentrate from Port Radium cobbed ore.

Sample 1 was prepared initially on a thin nickel disk by C.A. Josling of the Mines Branch Radiotracer Section following the procedure described by Nairn et al. (4).

Subsequently test samples were prepared from all five samples by L.G. Stonhill of the Research and Development Division of Eldorado Mining and Refining Limited, who utilized procedures described by Messrs. Glover and Rogers (5). The following details of the extraction treatment were supplied by Mr. Stonhill (letter dated April 6th, 1960):

> "Sample 1. Raffinate was extracted with tributyl phosphate, which was then contacted with a mixture of hydrochloric and hydrofluoric acids to re-extract protactinium. Aluminum chloride was added to this solution to complex fluoride, and any protactinium was extracted into benzene containing thenoyl trifluoracetone (TTA). This extract was evaporated onto a nickel disc."
>
> "Sample 2. Manganese dioxide was precipitated from the raffinate to act as a carrier. After dissolution of the carrier in hydroxylamine hydrochloride and nitric acid, protactinium was extracted into a benzene

> solution of TTA. From this it was re-extracted with an HF-HCl mixture and evaporated onto a nickel disc."
>
> "Sample 3. The P.R. concentrate was leached with nitric and hydrofluoric acids, the fluoride ion complexed with aluminum, and the protactinium carried on manganese dioxide. The procedure then followed in principle that described for Sample 2."
>
> "Sample 4. Any protactinium present was extracted from a nitrate solution with TTA in benzene. The organic extract was then treated as in Sample 2."
>
> "Sample 5. A protactinium concentrate was prepared as for Sample 2, in course of separating thorium from the ore."

The platinum dishes used were of the type used in preparing fluorimeter samples, and they proved rather unsatisfactory for the alpha-ray spectrometer because of their shape and small exposed surface area. The flat nickel disks used for Samples 1 and 2 proved much more satisfactory.

ALPHA-RAY SPECTRA

The alpha-ray spectra obtained for these samples were plotted out and are presented in Figures 1-6. Sample 2 is represented twice, in Figures 2 and 3,as it proved the most interesting and the only one with an unmistakable peak at 5.0 MeV which can be ascribed to Pa-231. Figures 4-6 show only the spectral region around 5.0 MeV, since this is the only part of the spectra of immediate interest.

Analysing the spectra in more detail, the following features are evident:

Figure 1 - Sample 1. The main feature of this spectrum is a broad peak centred at 4.65 MeV. This is clearly due mainly to ionium (Th-230) with an energy of 4.68 MeV. The low intensity under the uranium peak at 4.18 MeV indicates that little of the broadened peak can be due to U-234 at 4.76 MeV. Similarly there is only a small contribution from Pa-231 at 4.7 MeV, as shown by the low intensity at 5.0 MeV, although some Pa-231 is evidently present; however, both this Pa-231 peak and the Po-210 peak at 5.30 MeV are barely above background.

Figure 2 - Sample 2. This spectrum shows four well-resolved peaks. The most interesting peak is the third peak at 5.0 MeV, which is undoubtedly due to Pa-231. In addition the sample contained still appreciable uranium, as indicated by the U-238 peak at 4.18 MeV. The high middle peak, therefore, contains some U-234 particles at 4.76 MeV, some due to Pa-231 around 4.70 MeV, but this still leaves a fairly substantial residual peak which can be ascribed to Th-230 at 4.68 MeV. The fourth peak at 5.18 MeV can probably be ascribed to a broad peak due to some polonium background.

Figure 3 - Sample 2. This is a re-run of the sample after an attempt was made to thin down the sample layer to obtain better resolution. The same four peaks were obtained. The

apparent increase in the height of the U-238 peak at 4.18 MeV was traced to an increase in the background at that energy.

Figure 4 - Samples 3 and 5. Some drifting took place in the spectrometer discriminator level, as shown by the shift in the Po-210 peaks. Neither sample showed any significant count rate at 5.0 MeV above background.

Figure 5 - Sample 4. This spectrum exhibits a clear count minimum in the 5.0 MeV region indicating complete absence of Pa-231.

Figure 6 - Sample 5. This is a fuller spectrum for Sample 5 than that in Figure 4. Again there is no sign of any Pa-231 being present.

These spectra, therefore, indicate that some protactinium-231 was present in the concentrate extracted from the Port Hope raffinate, and possibly also in the concentrate from the Port Radium raffinate. None was found in the other three samples. These tests were run for identification only and no quantitative determination of Pa-231 is possible in the absence of precise information on sample weights and extraction yields.

Some further tests are in progress on ionium (Th-230) preparations. Some improvements in the technique of sample preparation are clearly desirable and are being considered.

REFERENCES

1. J.P. Hummel, F. Asaro and I. Perlman, Phys. Rev. 98, 261 A (1955)

2. B.G. Harvey, H.G. Jackson, T.A. Eastwood and G.C. Hanna, Can. J. Phys. 35, 258 (1957)

3. N.F. Moody, W.J. Battell, W.D. Howell and R.H. Taplin, Rev. Sci. Instr. 22, 555 (1951)

4. J.S. Nairn, D.A. Collins, H.A.C. McKay and A.G. Maddock, Proc. 2nd Geneva Conference on Peaceful Uses of Atomic Energy, 17, 216 (1958)

5. K.M. Glover and F.J.G. Rogers, Determination of Pa-231 by Alpha Energy Measurements, A.E.R.E. Report R 2971 Harwell, Berks., 1959.

- - -

GGE:CMcM/DV

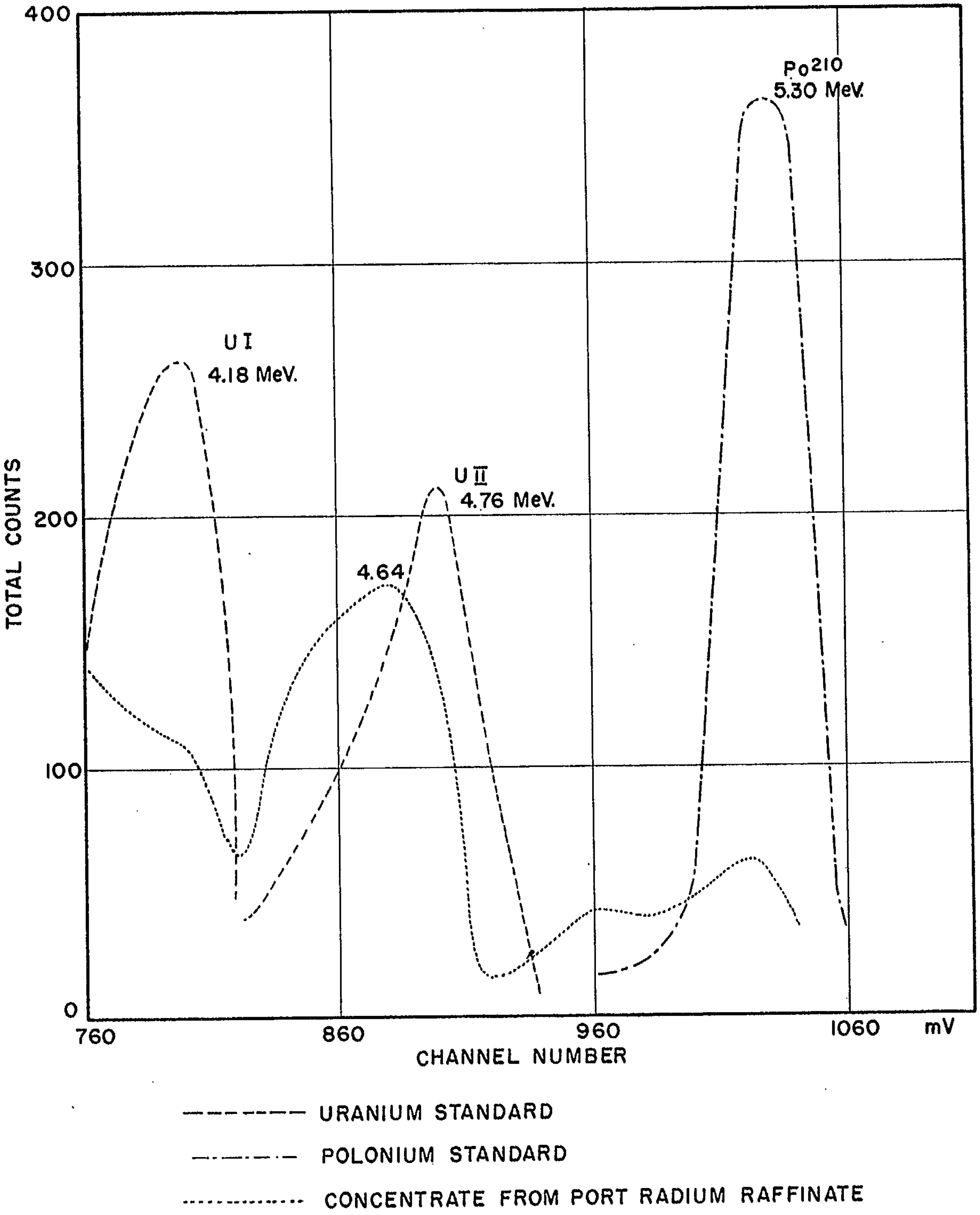
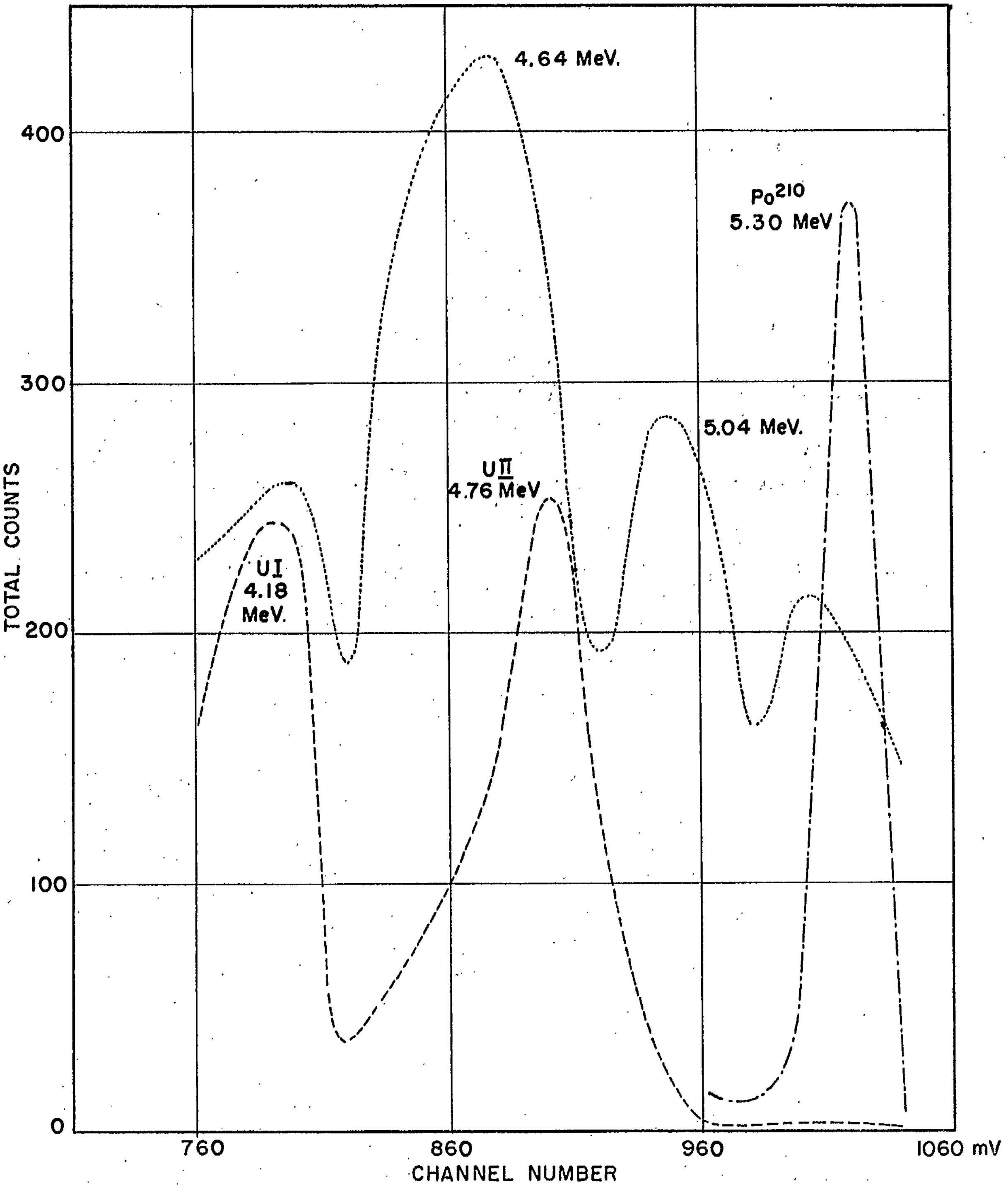


FIG I - ALPHA PARTICLE SPECTRUM OF CONCENTRATE OF PORT RADIUM RAFFINATE.



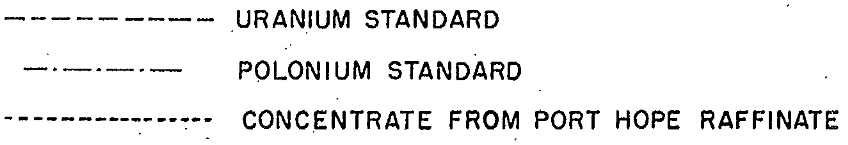


FIG 2 - ALPHA PARTICLE SPECTRUM OF CONCENTRATE OF PORT HOPE RAFFINATE.

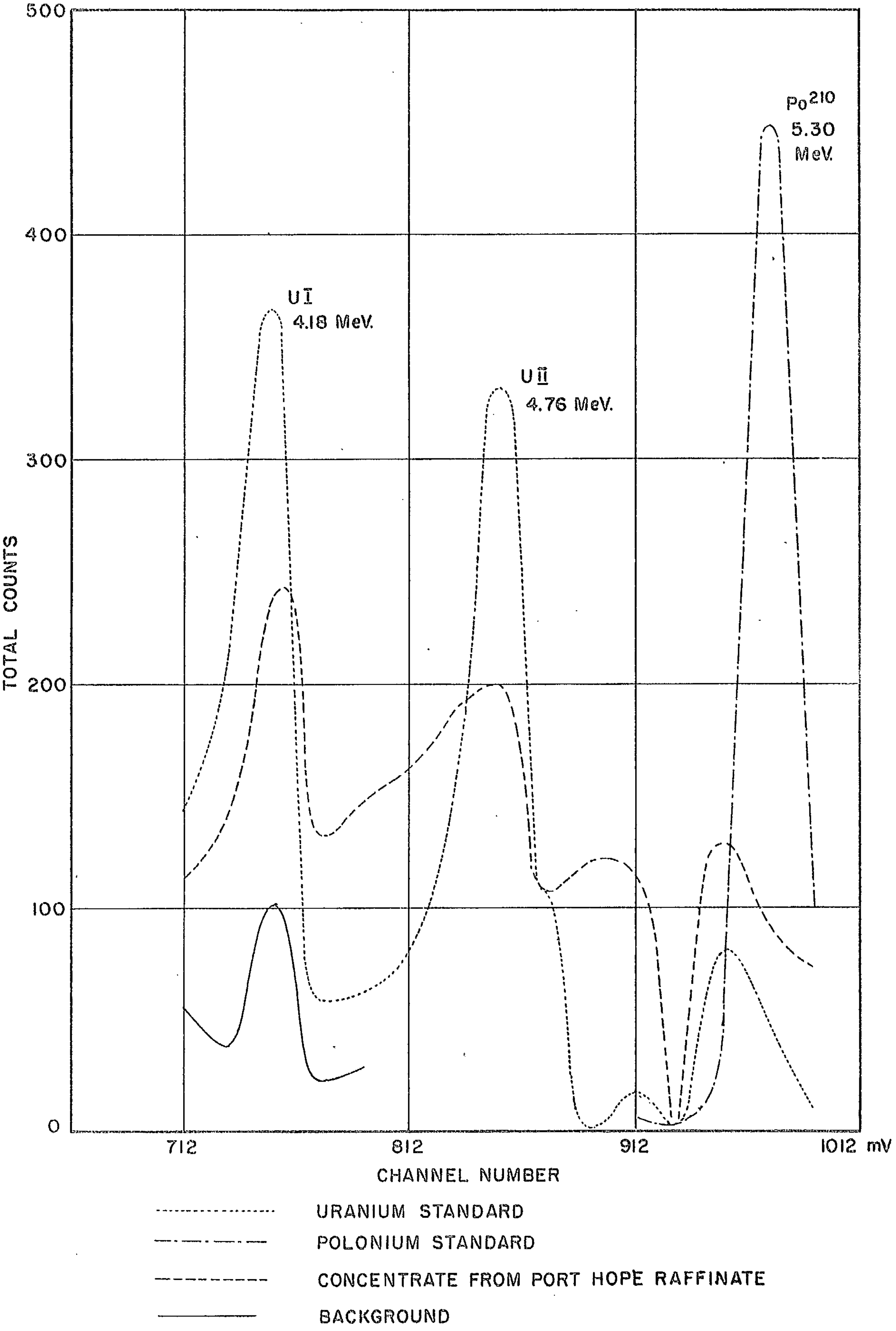


FIG. 3 - ALPHA PARTICLE SPECTRUM OF CONCENTRATE OF PORT HOPE RAFFINATE.

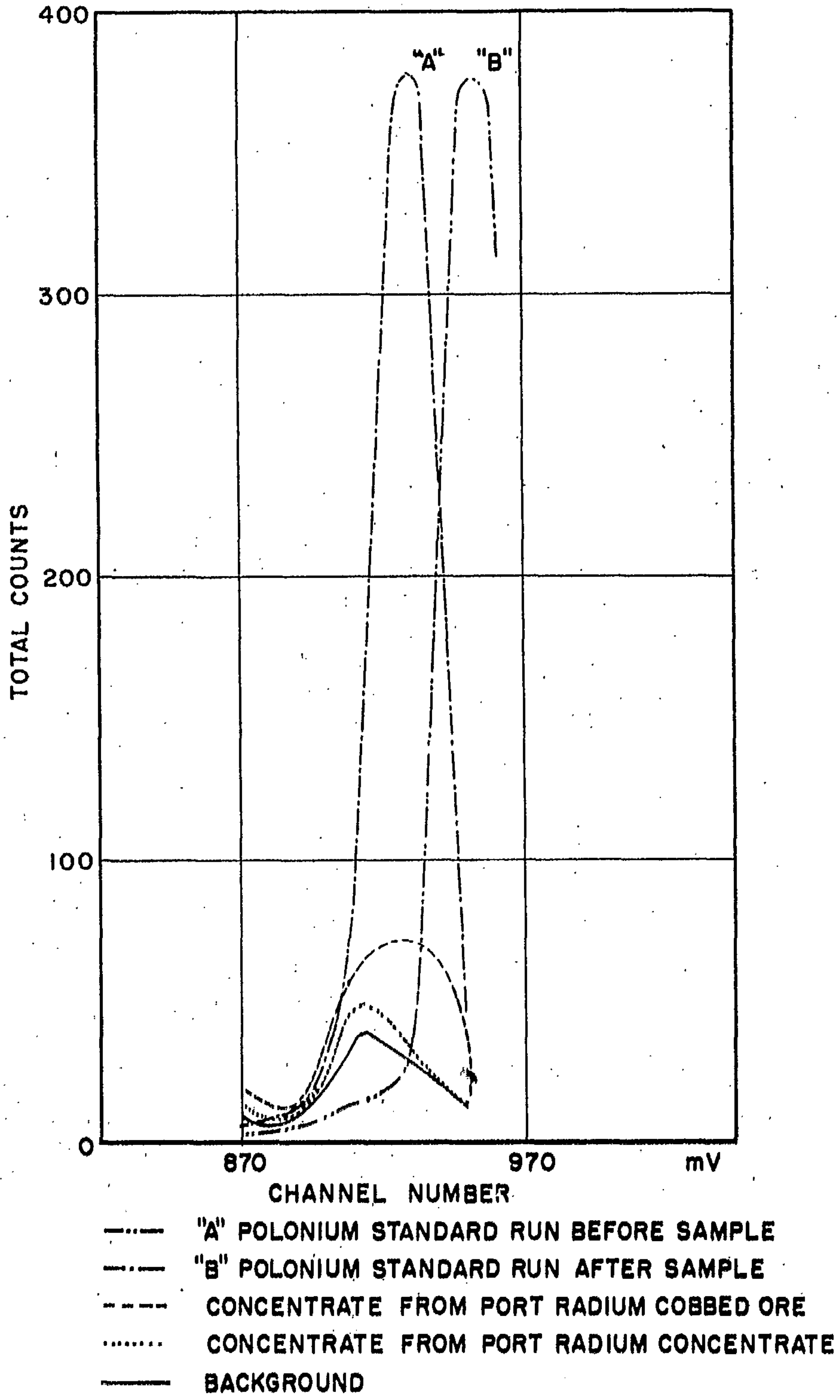


FIG 4 - ALPHA PARTICLE SPECTRUM OF CONCENTRATE OF PORT RADIUM CONCENTRATE & CONCENTRATE OF PORT RADIUM COBBED ORE.

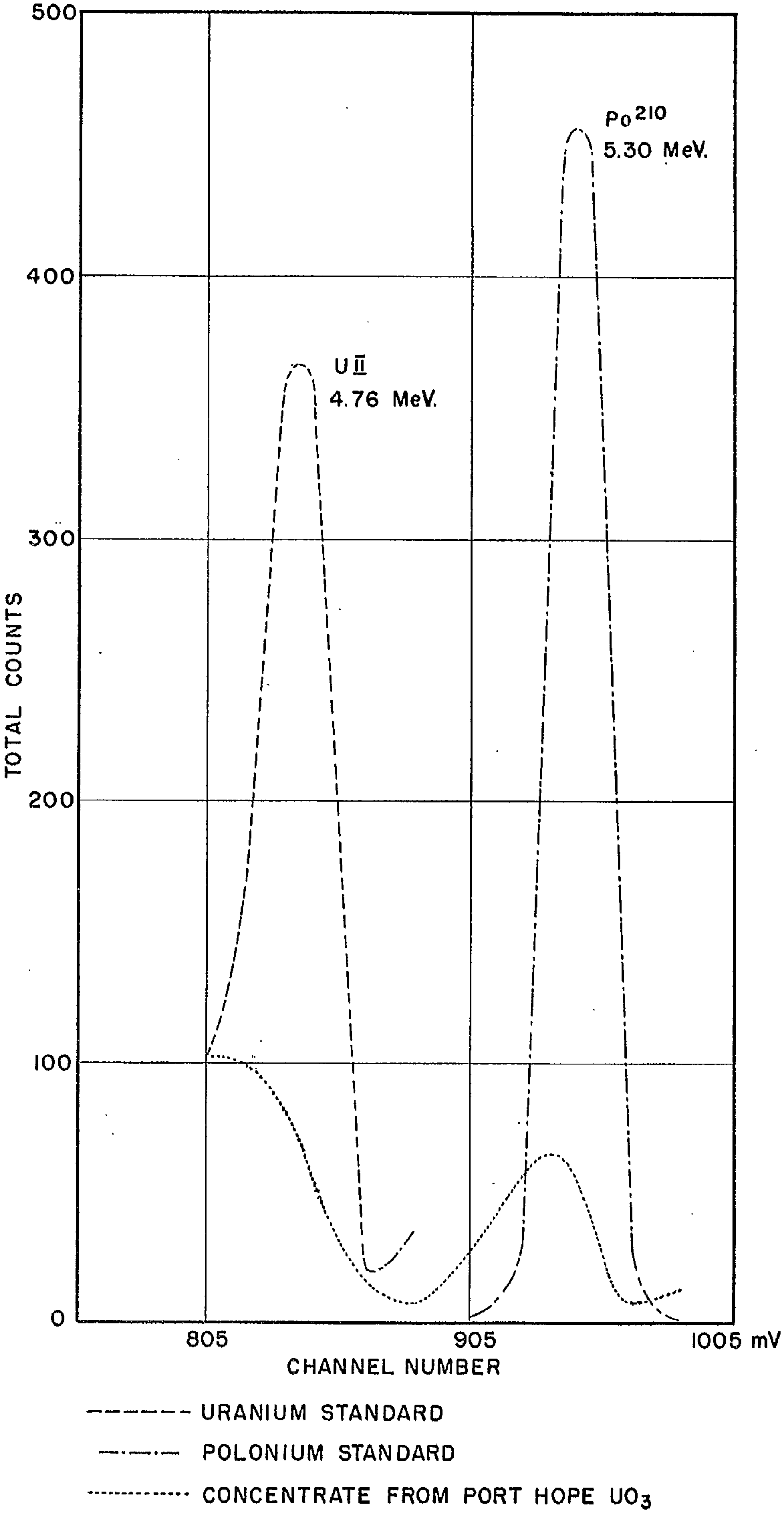


FIG. 5 - ALPHA PARTICLE SPECTRUM OF CONCENTRATE OF PORT HOPE UO_3.

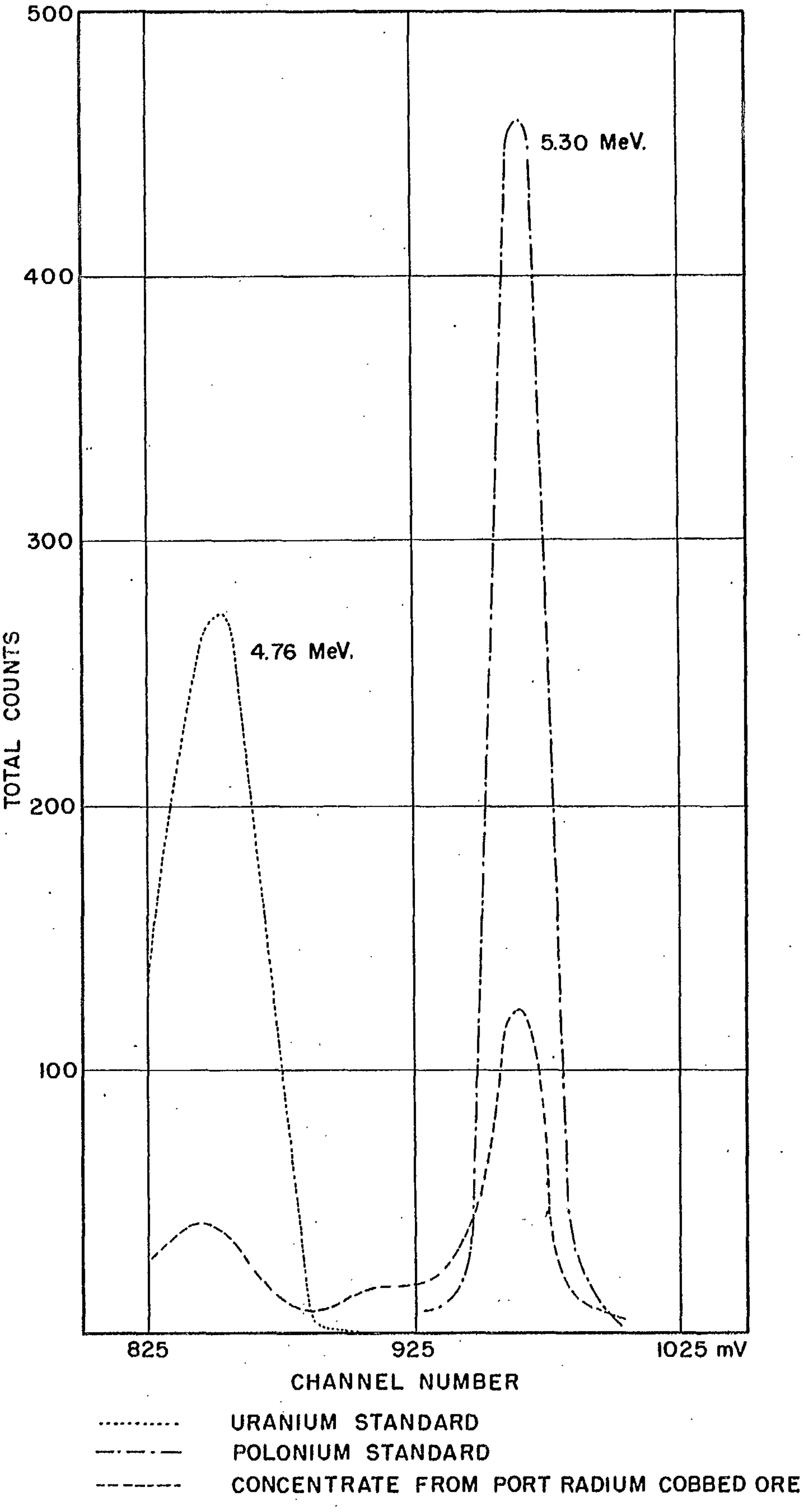


FIG 6 - ALPHA PARTICLE SPECTRUM OF CONCENTRATE OF PORT RADIUM COBBED ORE.