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Title: The Determination of Isotopic Uranium and Thorium Compositions in Marine Carbonates by Alpha Spectrometry

Speaker: Mary Mei-Ling Huang Cheng
Washington University
St. Louis, Missouri.

Abstract: Uranium and thorium in the sample solution are coprecipitated with iron and aluminum hydroxides. The separation and the purification of the two elements are done by solvent extraction and ion exchange. The purified element is then electroplated onto a planchet to form a very thin sample source for alpha spectrometry. The activities of the uranium and thorium isotopes are determined by alpha spectrometry using an "ORTEC" silicon surface barrier semiconductor radiation detector which is coupled through an "ORTEC" 101-201 low noise amplifier system to a "RIDL" 400 channel pulse height analyzer.

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IN NUCLEAR SCIENCE ABSTRACTS

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I will allot a few minutes for discussion after the talk, however, some of you may already have question in mind even before I start my presentation. When you look at the topic of my talk you may ask "Why do you determine isotopic thorium and uranium compositions in marine carbonates?", so let me answer this question first.

In nature there are 3 radioactive families as shown on the first slide. Uranium-238 decays by emitting alpha particle to thorium-234 which goes to protactinium-234 by beta decay and so on to stable isotope lead-206. When uranium is incorporated into a marine carbonate without its following products, the increase of the daughter elements can sometimes be used for age determination. Thus for example by measuring the ratio of thorium-230 to uranium-238 in coral limestone samples collected at various depths in drillings in Pacific atolls it has been possible to learn something about the geologic history of these deposits.

Alpha spectrometry is used for the isotopic thorium and uranium analysis. For alpha spectrometry, it is important to have very thin sources in order to get a good peak resolution of alpha particles. The electrodeposition technique is used for preparing these thin sources. It is also important to separate thorium from uranium because of the similarity in energy of the alpha-particles emitted by thorium-230 to those emitted by uranium-234.

The materials being analyzed contain very little uranium and thorium, often less than a few tenths of a part per million of each element. When sufficient material is available we started with a rather large sample, say 30 gm. The amount of uranium and thorium isolated for alpha pulse height analysis is at best a few micrograms.

The separation and purification procedures are summarized on the next slide, slide 2. A 10 to 50 gm. marine carbonate sample is dissolved with conc. HNO_3 and digested. Thorium-234 and uranium-232 tracers are added for yield determinations and about 10 mg. each of iron and aluminum are added as carriers. Centrifuge. The residue is boiled several times with conc. HNO_3 . The amount of the final residue which is mostly silicate material is very small. It has been shown that thorium and uranium in the residue is negligible, so no further analysis of the residue for thorium and uranium was made. At this point the volume of the solution is about a few hundred milliliters. To the solution ammonium hydroxide is added to precipitate iron and aluminum hydroxides and coprecipitate thorium and uranium. The precipitate is dissolved with about 10 ml. of 8 N HCl. This 8 N HCl solution is transferred onto the top of a Dowex anion exchange column. The column is washed with 8 N HCl. Th and Al come through the column and U and Fe are adsorbed on the column.

The next slide, slide 3, shows the adsorption of these elements from HCl on strongly basic anion exchange resin. (We will refer to nitrate system later.) In 8 N HCl soln. U is adsorbed on the resin and Th is not, so they are separated.

The next step is to purify each element. Could I go back to the previous slide, slide 2, please. Ammonium hydroxide is added to the 8N HCl effluent which contains Th and Al. The precipitate is dissolved with 7M HNO₃. This solution is transferred onto the top of a nitrate form anion exchange column. The column is washed with 7M HNO₃. Al comes through the column and Th is adsorbed on the column? On the right hand side of slide 3, the adsorption of Th and Al from HNO₃ on strongly basic anion exchange resin is shown. Back to slide 2 please. Th is eluted off the column with 1N HCl. U and Fe are eluted off the anion exchange column with 0.1N HCl. Iron is removed by isopropyl ether extraction from 8N HCl solution. Now we have Th and U purified, so the next step is to prepare thin source for alpha spectrometry. This is done by electrodeposition.

Slide 4: This slide shows the conditions under which Th and U are electrodeposited. During electrodeposition pH is adjusted to 2 with NH₄OH for Th and with 4M HNO₃ for U. The anode is a revolving coiled platinum and the cathode is a Pt planchet or a stainless steel planchet.

Slide 5: This slide shows the electroplating apparatus. The stirring motor and electrode holders are mounted on a sliding bracket which may be pushed up or down to adjust electrode position.

This is the assembled electrolytic cell and the next slide, slide 6, shows the component parts of the electrolytic cell. A planchet is held in place on the bottom of the glass cylinder by applying rubber cement between the contact surfaces. The heavy aluminum foil with a strip is used to make electrical contact between the planchet and the electrode holder of the Sargent electroplating apparatus.

The overall Th yield, as monitored by using the 24 day beta emitter thorium-234, is usually in the range of 80 to 100 %. As tracer for uranium, the 72 year alpha emitter uranium-232 is used. The uranium yield is usually about 50 to 90 %.

Now I'll talk about alpha-spectrometry. Slide 7 shows a block diagram of the equipment for alpha spectrometry. When an alpha particle passes through a semiconducting medium it produces electron-hole pairs. Electrons are raised to the conduction band and positive holes are left behind in the valence band. The presence of electric field causes the electrons and the holes to drift toward the positive and the negative electrodes

respectively. As a result, charge is induced in the external circuit and particle detection is made possible. The generated electrical pulses are proportional to the energy of alpha particles. The amplified signals are fed into the multichannel analyzer which records the number of pulses received in each energy interval. The data stored by the analyzer are read out by the IBM typewriter modified for this purpose.

The next four slides show the picture of the instruments.

Slide 8: This is the silicon surface barrier semiconductor detector. The sample holder can be raised up and down to adjust the distance between the detector and the source.

Slide 9: Vacuum chamber and ORTEC preamplifier.

Slide 10: ORTEC amplifier.

Slide 11: RIDL 400 channel analyzer and IBM typewriter.

Slide 12: This slide shows the alpha spectrum of Th isotopes. The time required for obtaining this spectrum was 17 hours. The peaks beyond channel number 170 are the peaks of thorium-228 daughters which have grown in.

Slide 13: This slide shows the alpha spectrum of U isotopes. The time required for obtaining this spectrum was 12 hours.

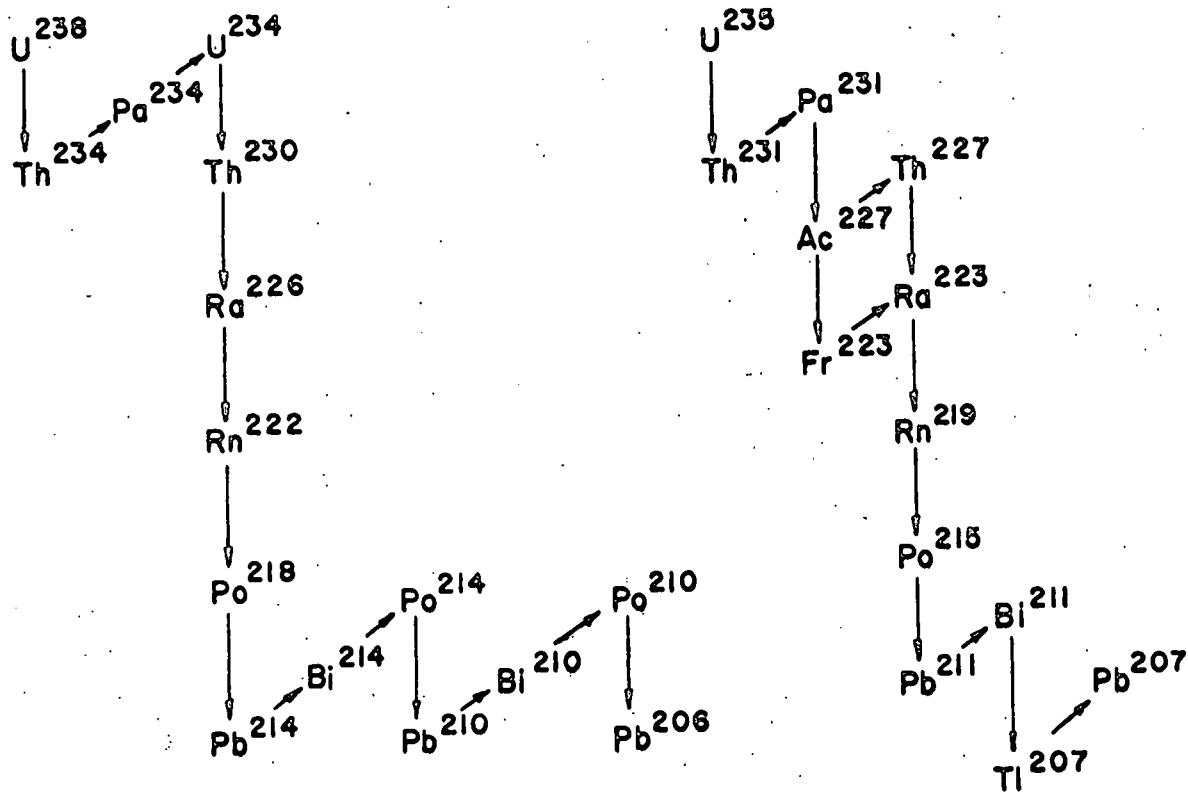
Slide 14: This slide shows the isotopic U compositions of some shell samples. These are modern and fossil shells from California, Russia and Alaska and the last one is Mississippian limestone standard which has been analyzed for isotopic Th and U by many laboratories across the country. An interesting point to observe here is that the U²³⁴/U²³⁸ activity ratio is usually not equal to 1.0 as one might expect it should be. This departure from the equilibrium value is real and the reasons for it are fairly well understood.

Slide 15: shows the isotopic Th compositions. Th²³⁰ content is related to age of carbonates. Th²²⁸ content is between 1 to 10 times 10⁻¹⁷ gm. per gm. sample. Such a low value can be obtained because thorium-228 has a rather short half-life (1.9 years) compared to thorium-232 and thorium-230. Thus the specific activity of thorium-228 is relatively high. You will note rather high uncertainties associated with most of the values listed. The amount of U and Th activity in these samples are extremely low and even with counting times of 10 to 20 hours statistical uncertainties are still high. In sample USSR-4 for example the total thorium alpha activity was 6 disintegration per minute. This under our solid state detector geometry is equivalent to about 1 count per minute. That means the counting efficiency of our solid state detector is about 20 %. Therefore, a rather long period of counting is necessary for each sample. Thank you for the slides.

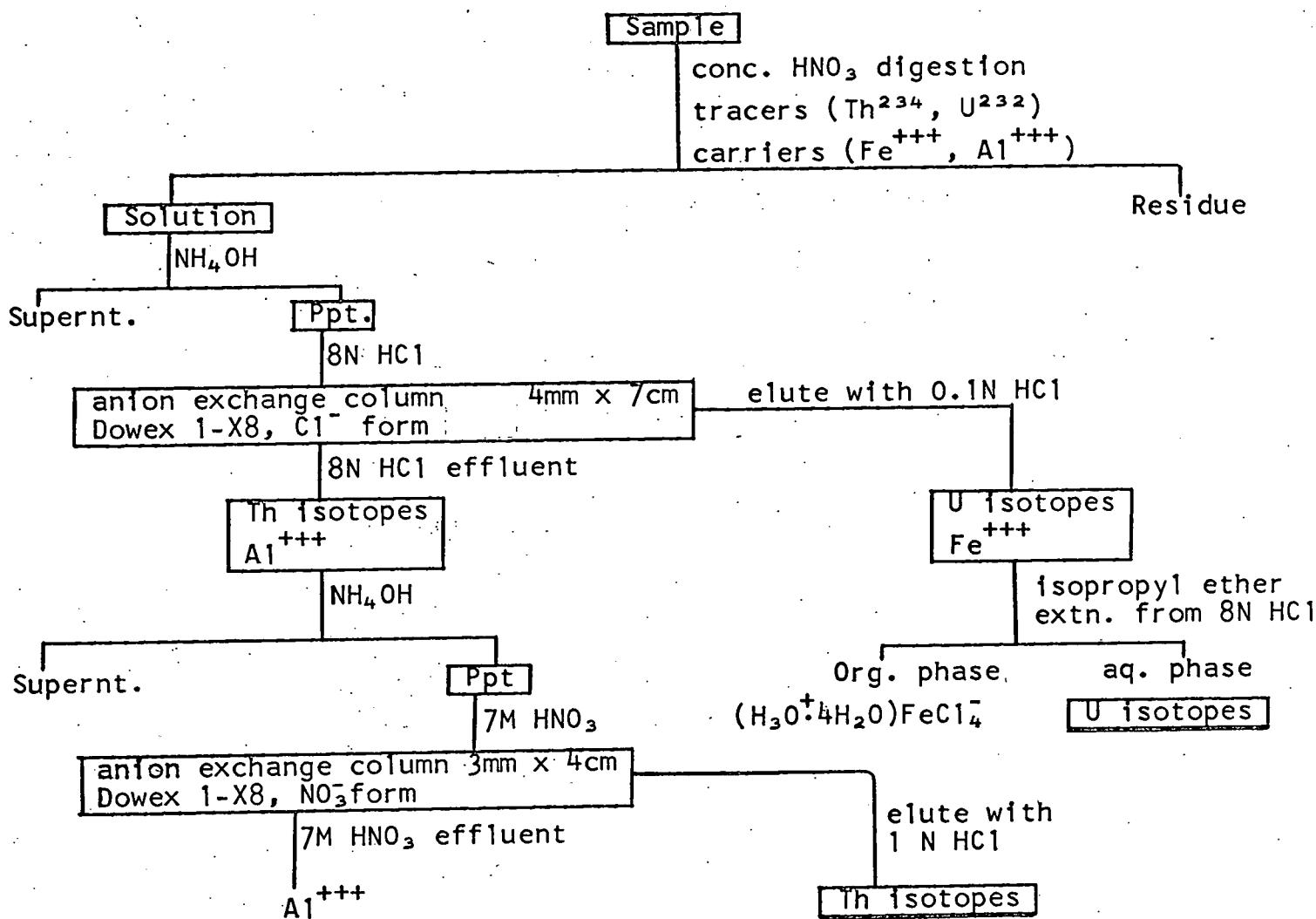
I'm indebted to Professor Potratz* who suggested the original problem and guided the research.

*Prof. H. A. Potratz, Department of Chemistry, Washington University, St. Louis, Missouri.

Uranium, Actino-uranium and Thorium Decay Series

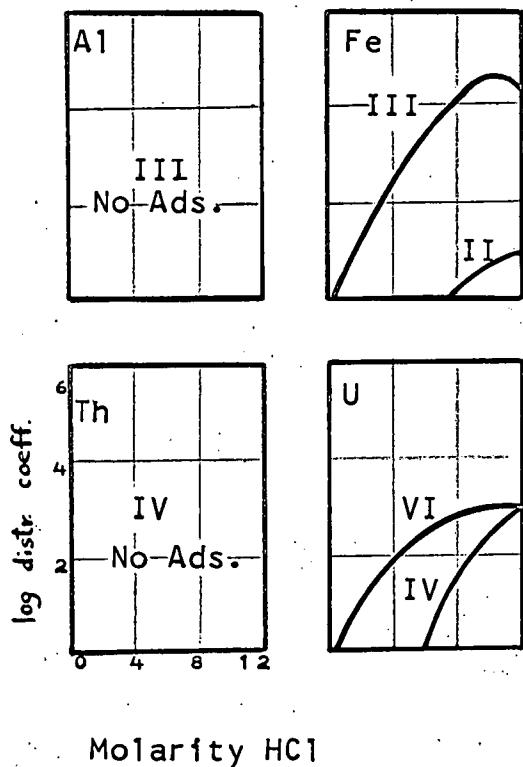


SEPARATION AND PURIFICATION OF Th AND U

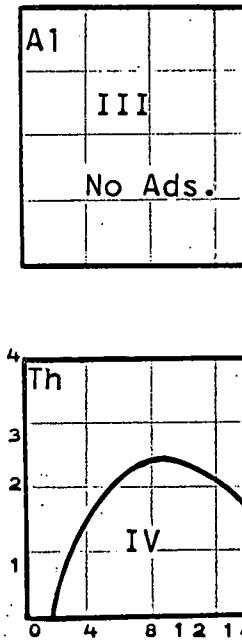


ADSORPTION OF Al, Fe, Th, AND U ON ANION EXCHANGE RESIN

FROM HCl



FROM HNO₃



Molarity HCl

(After Kraus and Nelson,
Proc. 1st Int. Conf. on
PUAE, Geneva, I, 113,
1955)

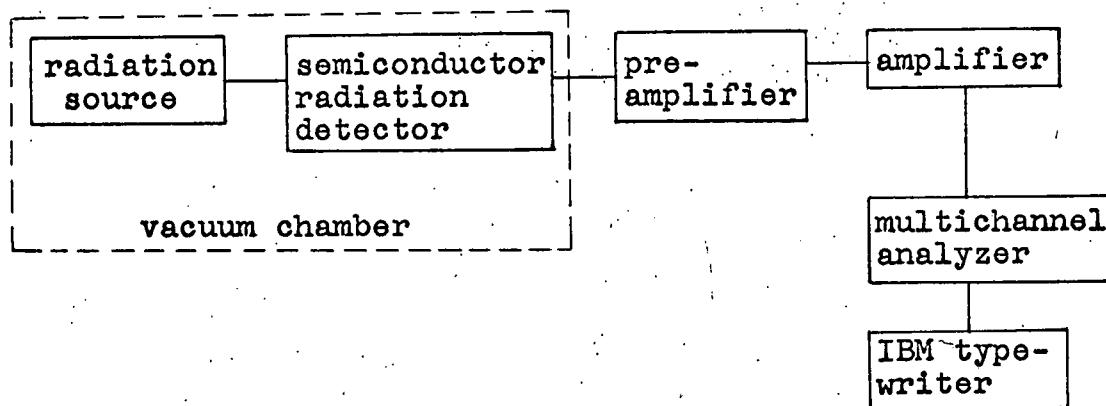
Molarity HNO₃

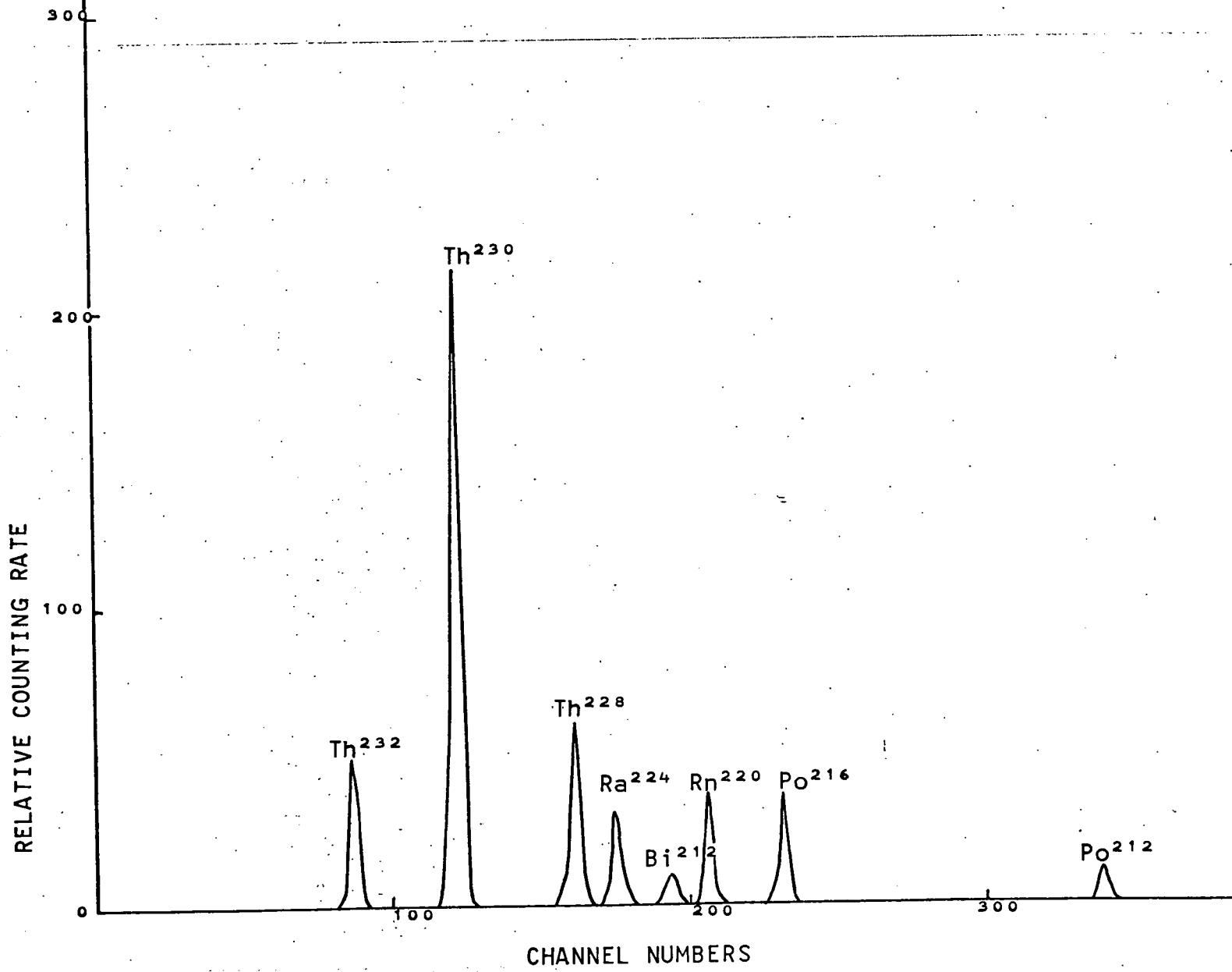
(After Buchanan and Faris,
Radioisotopes in Physical
Sci. & Ind., II, 361,
1962)

CONDITIONS FOR ELECTRODEPOSITION OF Th AND U

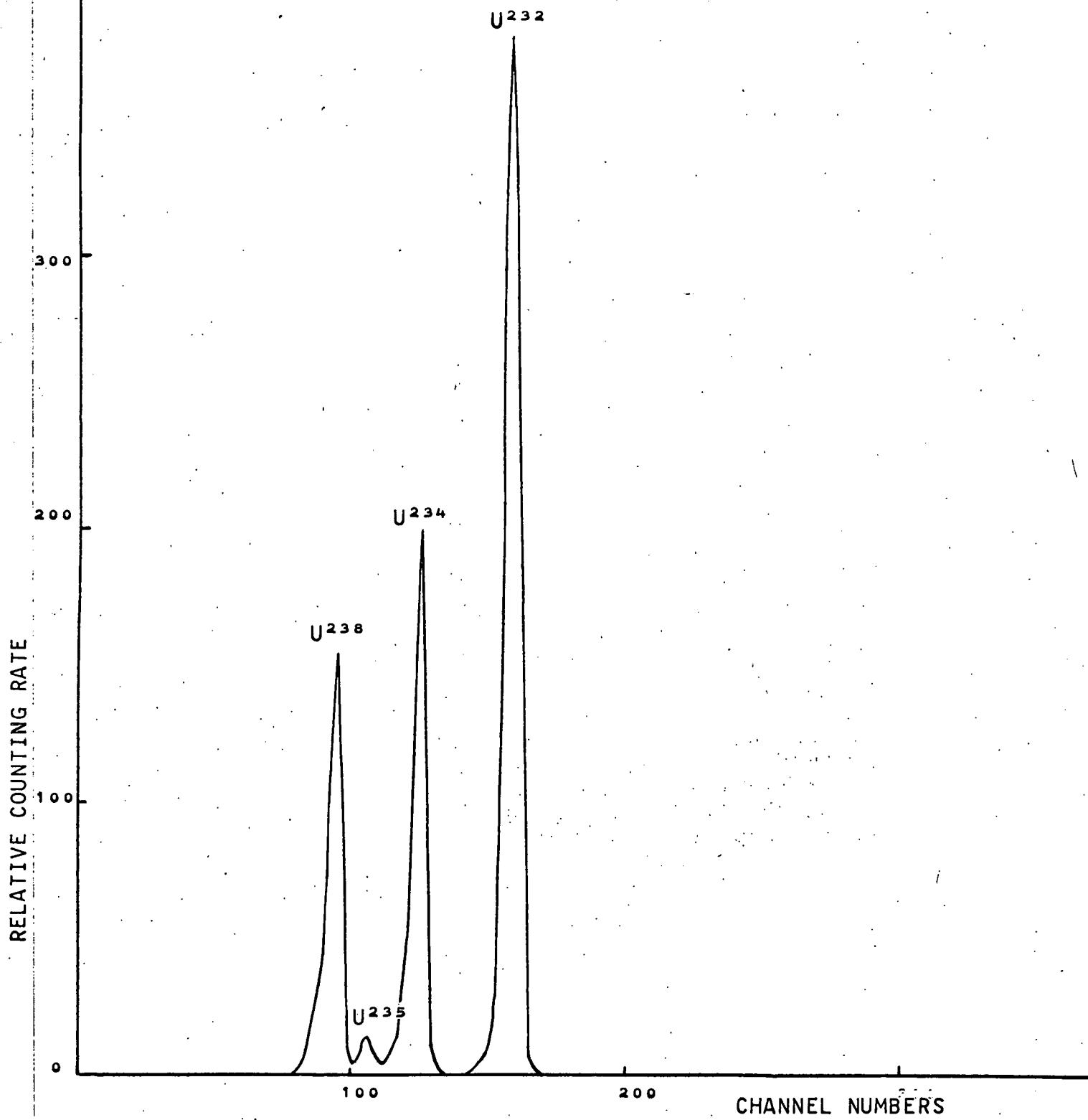
| | <u>Th</u> | <u>U</u> |
|---------------|--------------------------|----------------------------------|
| Electrolyte | Sat'd NH ₄ Cl | 4M HNO ₃ |
| pH (adjusted) | 2 | 2 |
| Current | 0.3 amp. | 1.5 amp. |
| Voltage | 3.5-4.0 v. | 6.0-6.5 v. |
| Time | 2 hrs. | 2 hrs. |
| Anode | coiled platinum | coiled platinum |
| Cathode | 1" dia. Pt planchet | 1" dia. stainless steel planchet |

BLOCK DIAGRAM OF ALPHA SPECTROMETRY





The Alpha-Spectrum of Thorium Isotopes Isolated
from Sample USSR-3.



The Alpha-Spectrum of Uranium Isotopes Isolated
from Sample BFMC-4.

| Sample Designation | Location of Collection | U CONTENT | | |
|--------------------|------------------------|-----------------------------|-------------------------------------|---|
| | | $\frac{U^{234}}{U^{238}}$ * | U^{238} (ppm) (fluorimetry) | U^{234} (ppm) (calculated) |
| BMMC-1(modern) | California | 1.27 (± 0.06) | 0.35 (± 0.01) | 2.4×10^{-5} (± 0.1) |
| BFMC-3(fossil) | California | 1.26 (± 0.04) | 1.60 (± 0.14) | $10. \times 10^{-5}$ ($\pm 1.$) |
| USSR-4(fossil) | Russia | 1.13 (± 0.05) | 0.31 (± 0.01) | 1.9×10^{-5} (± 0.1) |
| 62AMh24(fossil) | Alaska | 1.21 (± 0.10) | 0.10 (± 0.01) | 0.66×10^{-5} (± 0.08) |
| MLS #1(fossil) | Missouri | 1.02 (± 0.05) | 0.99 (± 0.04) | 5.4×10^{-5} (± 0.4) |

*indicates radioactivity

| Th CONTENT | | | |
|-----------------|--------------------------|---|--|
| | Th ²³² (ppm) | Th ²³⁰ (ppm) | Th ²²⁸ (ppm) |
| BMMC-1(modern) | <0.008 | 0.009×10^{-5} (± 0.006) | $\leq 0.33 \times 10^{-10}$ |
| BFMC-3(fossil) | 0.074 (± 0.008) | 1.50×10^{-5} (± 0.09) | 0.51×10^{-10} (± 0.04) |
| USSR-4(fossil) | 0.10 (± 0.01) | 0.43×10^{-5} (± 0.04) | 0.14×10^{-10} (± 0.02) |
| 62AMh24(fossil) | 0.31 (± 0.02) | 0.17×10^{-5} (± 0.01) | 0.95×10^{-10} (± 0.04) |
| MLS #1 (fossil) | 0.12 (± 0.03) | 1.65×10^{-5} (± 0.11) | 0.18×10^{-10} (± 0.03) |