Chemical challenges in the study of natural radioactive chains

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Natural radioactivity was first confirmed by chemical means, and for many years it was the only known form of radioactivity. Chemical techniques remain necessary for obtaining samples of series components on which detailed studies can be made. These techniques must contend with features peculiar to or emphasized in the natural decay series—low specific activities of long-lived parents and trace quantities of short-lived intermediates, interferences from carriers (isotopic or non-isotopic), and rapid growth of impurities in initially pure fractions. Examples of each of these features (challenges) are given.

Introduction

The enormous effort to study the radioactive decay process that is reflected in the series of *Table of Isotopes* (from the first edition in 1940 by LIVINGOOD and SEABORG[1] through the 7th edition by LEDERER and SHIRLEY)[2] has abated, and current efforts are concentrated on the heaviest elements, high spin states, etc. For the majority of nuclides, including the components of the natural decay series, continuing work primarily involves improved accuracy of existing properties and detection of less probable decay modes (which can be quite significant). Although the natural series share characteristics with, e.g., the decay chains among the fission products, they have important features that are not found in isolated nuclides—natural or otherwise.

In this report we concentrate on the thorium series (see Fig. 1) and the task of obtaining pure samples of individual components suitable for acquiring γ-ray spectra. This series is sufficient to illustrate the main characteristics of relevant chemical procedures. Students in the Undergraduate Research Opportunity Program at the University of Michigan participated in most of the work, and the research problems were chosen to illustrate chemical principles and radiochemical techniques. The components of the natural radioactive decay series represent many chemical groups – from alkali-like Tl and alkaline-earth-like Pb and Ra to high oxidation state Th, Pa, and U – that illustrate the periodic table. Most of the chemical procedures – precipitation, solvent extraction, and chromatography – are prescribed in the National Academy of Science monographs on radiochemistry[4] and are accessible to relatively inexperienced chemists. In this paper we report those features that turned out not to be so simple and that made our lives interesting.

Radiochemical challenges

Low specific activity

That the natural decay series still exist in nature derives from the long half lives of the parents, which must in turn have small activity/mass ratios. For ^{232}Th the specific activity is about 0.11 μCi/g ($4.06 \cdot 10^3$ disintegrations per second per gram). Samples of sufficient activity for study of low intensity features are so massive that low energy β- and γ-radiations are severely attenuated. In addition, moderate energy β- and γ-radiations fluoresce the bulk material and give rise to radiations that are not directly produced by decay.

We began with studies of ^{228}Ra. This nuclide was extracted[5] from several hundred grams of thorium nitrate. Once we had prepared the roughly 10 liters of Th(NO$_3$)$_4$ in tri-butyl phosphate (saturated with concentrated nitric acid) from which we extracted crude ^{228}Ra with nitric acid, we wanted to save it for repeated milkings. Unfortunately, over a period of years the TBP decomposed, producing free phosphate and forming an insoluble mass with the thorium.

In some ways low specific activity can be useful. We have used a cupferron extraction[6] of ^{234}Th from a weighed sample of uranium to prepare a radioactivity standard (source with known disintegration rate). The low specific activity of ^{238}U permits its atoms to be counted by weight. At equilibrium, the ^{234}Th has the same activity, albeit in very small mass ($1.44 \cdot 10^{-11}$ that of U). We are completing measurements on ^{234}Th to make it an absolute standard for X- and γ-rays.
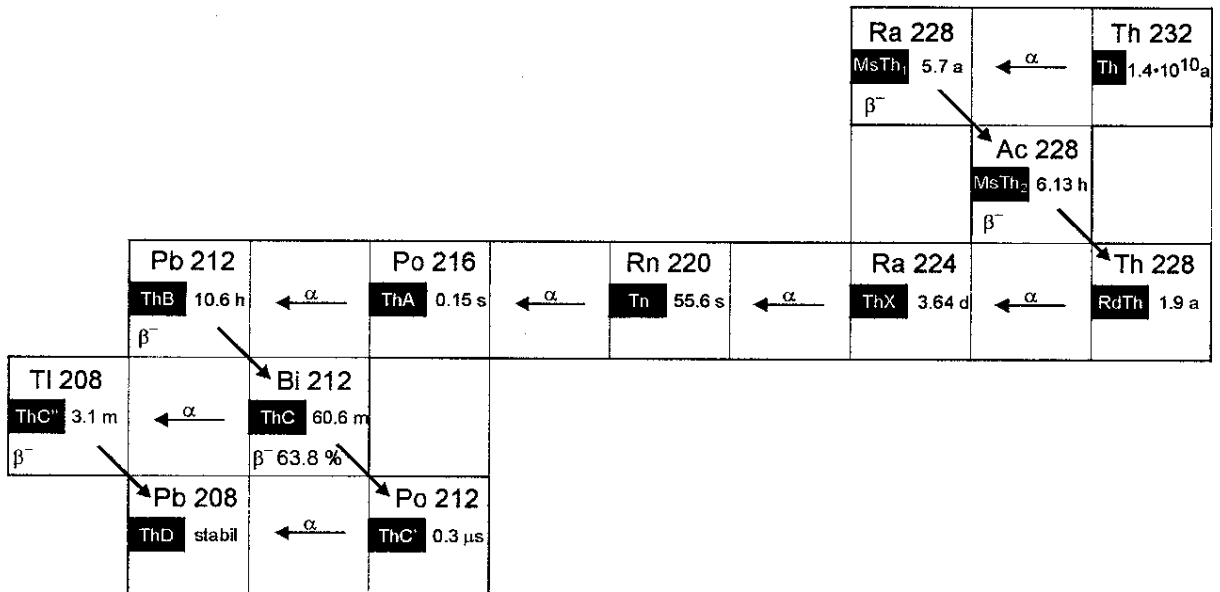
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Fig. 1. Diagram of the thorium series taken from Ref. 3

Isotopes of a given element

An important feature of the natural radioactive chains that is not found in the beta decay chains (such as fission products, which, however do have isotopic components in different chains) is the occurrence of two or more isotopes of an element at different positions in the chain. For example the ^{232}Th chain includes ^{228}Th as well as the chain parent, ^{228}Ra as well as ^{224}Ra, and two short-lived isotopes of polonium. Fairly pure samples of ^{224}Ra can be produced by quantitatively removing radium from thorium, then separating radium again a few days later. The minimum 228/224 ratio obtains after a short growth period. At that time it is 0.17%. A more practical growth period of 3.7 days (one half life of ^{224}Ra) gives 0.24%.

Getting pure ^{228}Ra is more complicated. The initial activities of ^{224}Ra and ^{228}Ra are the same when they are separated from thorium in equilibrium with all of its decay products. Obviously the 3.66-d ^{224}Ra dies away more quickly than the 5.76-y ^{228}Ra, but the growth of ^{224}Ra as a descendent of ^{228}Ra substantially halts the loss of ^{224}Ra after about 3 weeks. (There is a broad minimum at about 3% in the 224/228 ratio 3–6 weeks after chemical separation, after which the ratio increases. The exact dependence can be obtained with the four-member Bateman equation for the chain from ^{228}Ra to ^{224}Ra.)

Only by repeated removal of the 1.9-y ^{228}Th growing into the mixture can chemically isolated ^{228}Ra have higher purity. For example, if subsequent purifications are made after 19, 26, and 31 days, at about 35 days the ratio reaches about 0.15%.

If very pure ^{224}Ra is desired, the ^{228}Th removed in the purifications of ^{228}Ra can be used. Unless this is planned and carried out over a period of several years, the activity levels will be relatively low.

We set up a schedule of ^{228}Th removals designed to yield <0.1% ^{224}Ra in ^{228}Ra. The ^{228}Ra was intended for a study of photon (X- and γ-rays) spectra, for which we had found 7–10 ml volumes to be most appropriate Therefore about 10 ml of radium in 0.01M acetic acid was kept in a 20-ml liquid scintillation vial. "Cleanup" involved pouring the contents into a separatory funnel containing an equal volume of 0.01M HDEHP (bis-2-ethylhexyl-orthophosphoric acid) in heptane, shaking for 20–30 seconds, and draining the cleaned radium solution back into the scintillation vial.

The effectiveness of a particular purification is not immediately evident. For purposes of assay the most useful radiations[7] of ^{228}Th are γ-rays of 84.3 keV (1.2%) and 215.8 keV (0.28%); the former is in the energy region dominated by K X-rays, and the latter is weak relative to the Compton continuum of higher energy ^{228}Ac γ-rays. In order to detect small amounts of ^{228}Th it is necessary to await the growth of descendants, and under those conditions it is easiest to use the 43% 238.6-keV γ-ray of ^{212}Pb. Because of the delay we did not always monitor the effectiveness of each separation, but it soon became apparent that reduction in the amount of ^{224}Ra in the mixture was not as great as expected.

We assayed all of the fractions involved in the procedure and discovered that when the radium solution was poured out of the liquid scintillation vial, essentially all of the ^{228}Th remained on the walls of the vial. We found that it could be removed by rinsing the vial with the HDEHP extractant and hypothesize that the Th is held in a thin coating of oily HDEHP deposited on the walls from the acetic acid solution after the first solvent extraction cycle.

Subsequently, we simply poured the acetic solution into a clean vial when removal of Th was needed. Other cases of unexpected chemical results which arose form the small mass of some intermediates are given in the following section.

High specific activity

In the original preparation of our ^{228}Ra source material, we planned to use an anion exchange resin in the hydroxide form as the last step. Such a column had been reported[8] to trap all (aged) fission products except Sr and Cs (plus the rare gases). (Note that there are no long-lived fission products of Rb or Ba and radioactive forms of these elements would not have been present in the "aged" fission products.) We expected Ra to behave like other alkaline earths and anticipated that we could remove residual Th and Ac and obtain a quite pure Ra. However, we neglected to consider the cation exchange capacity of an "anion" column. The Ra did not elute as expected, and only by increasing the ionic strength of the solutions were we able to obtain Ra more or less as expected. In retrospect, even if the column had worked as desired, it would have been difficult to transfer very pure water containing very pure Ra among containers without leaving significant amounts or Ra attached to the cation exchange sites in those containers.

An obvious feature of high specific activities is that precipitation steps cannot be used without adding carrier. However, for most measurements the presence of carrier, and particularly isotopic carrier, is a serious interference. Other chemical techniques are better.

X-rays and other low energy radiations

The Ge(Li) detectors used in much of the detailed spectroscopy of radioactive materials in the 60s and 70s had dead layers (from Li diffusion) that absorbed low energy photons before they could reach the sensitive volumes of the devices. One goal of continuing studies of these nuclides is to characterize the low energy photons emitted in the decay. Gamma-rays can (generally) be assigned to the appropriate nuclide even when the sample contains several nuclides. This is not the case with X-rays, particularly L X-rays. The L X-rays for $80 < Z < 93$ (i.e., components of the natural decay series) are complex when observed with detectors typically used with radioactive materials. In principle more than ten discrete transitions[7] contribute to the spectrum of a given element, although in practice four or five transitions dominate. These transition interleave with those of neighboring elements, such as the parents and descendants in decay series. The relative intensities of these dominant components depend on the mechanisms of producing the L vacancies. When two or more nuclides contribute to the X-ray spectrum, it is generally impossible to determine the spectrum of each nuclide. Therefore, chemical isolation of a particular member of a chain is necessary in order to record the X-ray portion of its spectrum.

The final form of the sample is important. The half thickness[2] of water for 10 keV photons is about 1.4 mm. It is convenient to work with solutions when a series of separations will be required, but these factors show the volumes must be small and the containers must be relatively transparent to the radiations of interest. We have found foamed plastic "coffee cups" to be good containers of aqueous solutions of 5–10 ml volumes.

Carrier effects

When carriers, particularly isotopic carriers, have been used to aid in isolating a particular product, fluorescence of the carrier produces X-rays that contribute to the spectrum. Even non-isotopic carriers must be used with care. The absorption of low energy radiations depends strongly on the atomic number of the absorber. Barium carbonate is an effective carrier for lead, but Ba could interfere with detection of low energy (<15 keV) radiations from radioactive lead. It may be useful to substitute a less efficient carrier, such as calcium carbonate, is order to reduce the attenuation effects from the carrier.

Atomic recoil

In order to obtain a gamma-ray spectrum of 3-minute ^{208}Tl with good statistics and little distortion from summing and pulse pileup, we used a pair of ion exchange columns to give a fairly steady supply of ^{208}Tl. In dilute HCl bismuth forms an anionic complex that is strongly held on an anion exchange resin.[9] Thallium remains cationic. ^{212}Bi was loaded onto an anion column placed just outside the shield of the γ-ray detector. Dilute HCl was pumped through the column and to a small cation column placed inside the shield in a suitable counting position. The second column caught the ^{208}Tl eluted from the first. It worked very well, and we could easily replenish 60-min ^{212}Bi, which could be milked from 10-hour ^{212}Pb.

Then we tried to use the same chemistry to get the spectrum of pure ^{212}Bi, that is, to wash Tl from Bi on an anion column in counting position. It did not work.

We correlated the Tl contribution to the gamma-ray spectrum with flow rate and concluded that a portion of the Tl – about 30% – was not accessible to the acid flush. We changed the eluant to water, which removed the Bi, and showed that approximately this 30% of the Tl remained on the column. The most likely cause of the retention is that about 30% of the Tl recoils (from alpha-decay of Bi atoms on the surface of the ion exchange resin) are embedded in the resin matrix and are not in equilibrium with the eluant.

Hot atom chemistry

The chemical properties of a component in a chain can depend on the environment in which it was created. We made a "cow" by extracting ^{228}Th into 0.01 M HDEHP in heptane and milking Ra-Pb with dilute acid. That worked quite well. Then we decided to obtain a gamma-spectrum of the ^{228}Th by washing the decay products from the organic phase. (Bismuth is partially extracted by HDEHP, but it is a remote descendent of Th and it decays fairly quickly after the Pb parent is removed.) Although the procedure should have worked

based on the chemical properties of each of the elements in the aqueous solutions, there was a small amount of residual Pb that could not be removed from the organic phase by washing. We attribute this residue to organometallic forms of Pb that preferentially dissolved in the heptane. These forms presumably arose from chemical reactions between the recoiling ^{212}Pb (produced by α decay of ^{216}Po) and heptane.

Short half-lives

Earlier studies[10] of the radiations of ^{228}Ra involved considerable delays between purification and counting. It was necessary to infer the radiations of ^{228}Ra by comparing spectra obtained after various growth periods. Unfortunately, the shortest growth periods were a few hours, and small differences were sought in large numbers. With solvent extraction and small volume sources, we were able to begin taking spectra about 30 seconds after purification. These spectra (see Fig. 2) showed that all but one of the 8–40 keV lines attributed[7,10] to ^{228}Ra were instead due to ^{228}Ac.
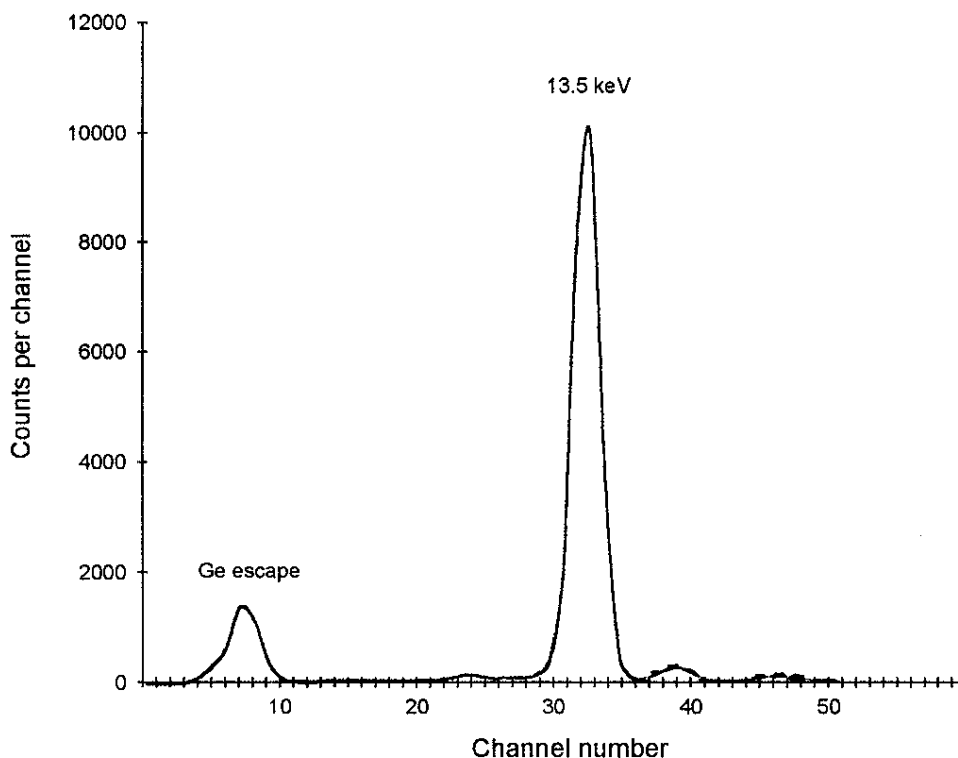

Fig. 2. Gamma-ray spectrum of ^{228}Ra. The source was dissolved in about 10 ml of dilute acetic in a foamed plastic cup. It was about 3 cm above a Be-windowed intrinsic Ge detector. Counting began about 60 seconds after removal of impurities, in particular ^{228}Ac. The dashed (upper) curve is the raw spectrum; the solid (lower) curve is corrected for the growth of a 6.15-h descendent

Discussion

Although the natural radioactive series have been studied for more than 100 years, there are many interesting details yet to be determined with modern instrumentation. While one must marvel at the skill and ingenuity of the "pioneers" who characterized these nuclides in the early days, new techniques, including chemical techniques, must be developed in order to make full use of the power of these instruments.

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