DETERMINATION OF $^{226}$Ra AND $^{230}$Th

AN IMPROVED PROCEDURE

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(Received June 23, 1983)

Separation and isolation of radium and thorium by successive coprecipitation on BaSO$_4$ is usually both fast and reliable, but suffer from both cross contamination (of Ra by Th) and low recovery (of Th) in the presence of some common components of environmental samples. An alternative method, free from these problems, involves the use of La$^{3+}$ as holdback carrier for Th$^{4+}$ during precipitation of Ba(Ra)SO$_4$, followed by carrying of Th$^{4+}$ on LaF$_3$. Yields are found to be high in several cases which were troublesome by the other method.

Introduction

Environmental radioactivity surveys focus primarily on radium and thorium, although radon, polonium, lead and bismuth are also of concern. While several radioisotopes of radium and thorium are of interest environmentally, the two most commonly of concern are $^{226}$Ra and its precursor $^{230}$Th, being directly associated with all uranium mining operations. Others, such as $^{228}$Ra, $^{228}$Th, $^{224}$Ra and so on, are produced only where deposits of thorium accompany those of uranium.

Common methods for determination of radium and thorium in environmental water and soil samples usually involve the use of Ba$^{2+}$ as carrier for Ra$^{2+}$, when precipitated as BaSO$_4$. A number of methods are available for radiochemical thorium determination$^{1,2}$ but the simplest and most elegant is through the use of BaSO$_4$, which carries thorium (and several of the transuranic elements) when sufficient K$^+$ ion is added to the solution$^{3,4}$.

There are, however, two problems with this method. Firstly, in the presence of even small concentrations of certain polyvalent cations – Fe$^{3+}$, Al$^{3+}$ and numerous others – Th$^{4+}$ is incompletely carried by BaSO$_4$ unless very large concentrations of K$^+$ are used.$^{3-6}$ Some other contaminants which cause serious loss of Th have not yet been identified. The second problem, related to the first, is that in samples which contain high concentrations of K$^+$ (or of NH$_4^+$ or Na$^+$) $^{230}$Th will be carried
along with Ra$^{2+}$ in the first BaSO$_4$ precipitation. This is a serious problem, since $^{226}\text{Ra}$ and $^{230}\text{Th}$ are in practice indistinguishable by α spectroscopy, which is the usual way of measuring these radionuclides. To measure the growth of radon and its daughters is not usually convenient because, since some Rn is usually incorporated in the BaSO$_4$ anyway, the measurement would have to be done only after several days’ growth to distinguish $^{226}\text{Ra}$ from $^{230}\text{Th}$ reliably.

During the course of an investigation of the effects of various impurities on the carrying of trace amounts of Th$^{4+}$ by BaSO$_4$, we have developed an analytical procedure for determining $^{226}\text{Ra}$ and $^{230}\text{Th}$ on a single solution which alleviates the above problems and at the same time is not as time consuming as solvent extraction or ion exchange procedures. The method is based on the well known ability of LaF$_3$ to act as a carrier for many elements, and on the fact that La$^{3+}$ is a strong interference in the carrying of Th$^{4+}$ by BaSO$_4$.

The method, in essence, involves addition of Ba$^{2+}$ and La$^{3+}$ carriers for Ra$^{2+}$ and Th$^{4+}$, respectively. Precipitation of BaSO$_4$ carries all of the Ra$^{2+}$, while La$^{3+}$ prevents coprecipitation of Th$^{4+}$. Subsequent precipitation of LaF$_3$ carries all of the Th$^{4+}$. Mechanical losses (loss of crystals in the filter chimney, adsorbed on the glass vessels, and so on) are expected when the total precipitate weighs less than 2 mg. Thus, $^{133}\text{Ba}$ and $^{234}\text{Th}$ were used as tracers to indicate the physical recovery. Chemical losses were found to be negligible.

**Experimental**

Most reagents were of the best available analytical grade and were used without further purification. The tracer $^{133}\text{Ba}$ was obtained from Amersham Corp., while $^{234}\text{Th}$ was extracted by water-ether partition using a nitrate solution of UO$_2^{2+}$ and purified by anion exchange. A stock solution of $^{226}\text{Ra}$ was obtained from the National Bureau of Standards, Washington, USA and the $^{230}\text{Th}$ solution was obtained from Oak Ridge National Laboratories, USA. Ra was made up in 1M HCl solution and Th in 1M HClO$_4$.

Measurements of γ-ray activity were made using a 3 × 3 inch NaI scintillation spectrometer system integrating over the 63 and 93 keV peaks of $^{234}\text{Th}$ and the 356 and 382 keV peaks of $^{133}\text{Ba}$. The α activities $^{226}\text{Ra}$ and $^{230}\text{Th}$ were measured using silicon surface barrier detectors in an α spectrometer system, integrating over the 4.7 MeV and 4.8 MeV peaks of $^{230}\text{Th}$ and $^{226}\text{Ra}$ respectively. Given thick (≥0.5 mg · cm$^{-2}$) samples, the resolution was scarcely better than 0.2–0.3 MeV, so that the 5.3 MeV α peak from $^{222}\text{Rn}$ was often found to interfere with measurements of $^{226}\text{Ra}$. Consequently, the quantity of barium carrier used was always kept