A COMPARISON OF METHODS FOR THE DETERMINATION OF THE DATING-NUCLIDES $^{210}\text{Pb}$ AND $^{226}\text{Ra}$

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(Received November 13, 1992)

Lead-210 is often used to date recent (≤ 100 y) environmental samples. Three different methods for its determination are compared: $^{210}\text{Pb}$ $\beta$-counting with a low level proportional counter, $^{210}\text{Pb}$ $\gamma$-spectroscopy and $^{210}\text{Po}$ $\alpha$-spectroscopy. Agreement within analytical errors was found for the three methods in two sediment cores from Lake Zurich, Switzerland and in IAEA SD-A-1 deep sea reference material. For $^{210}\text{Po}$ $\alpha$-spectroscopy, the detection and determination limit is an order of magnitude lower than these for the other methods. Methods for the determination of $^{226}\text{Ra}$ are also discussed. Measurements on low level proportional counters are difficult to interpret and not suitable for routine work. A better way to measure $^{226}\text{Ra}$ is $\alpha$-spectroscopy of colloidal Ba(Ra)SO$_4$.

Due to its half-life (22.3 y) $^{210}\text{Pb}$ is a suitable dating nuclide for relatively recent samples and has found numerous applications (e.g., References 1–4). It results from the decay of $^{222}\text{Rn}$ in the atmosphere (unsupported $^{210}\text{Pb}$) and from the decay of $^{226}\text{Ra}$ inherent (supported $^{210}\text{Pb}$) to the samples. For dating purposes, only the unsupported part can be used. The total $^{210}\text{Pb}$ activity can be determined by direct counting of its 46.5 keV $\gamma$-line, by $\beta$-counting of the 5.01 d half-life daughter $^{210}\text{Bi}$ or by measuring the $\alpha$-emission of its granddaughter $^{210}\text{Po}$. Gamma spectroscopy has the advantage of a non-destructive method, but this technique needs corrections for self-absorption of $\gamma$-rays in the sample matrix if absolute measurements are performed. Another disadvantage is the low emission probability of the $\gamma$-line (only 4.26%). Beta-counting is more sensitive but the preparation of radiochemically pure $^{210}\text{Pb}$/$^{210}\text{Bi}$ sources is relatively time consuming. The most sensitive method is $\alpha$-spectroscopy of $^{210}\text{Po}$, but in very recent sediments equilibrium between $^{210}\text{Pb}$ and $^{210}\text{Po}$ is not always reached. In order to assess the unsupported $^{210}\text{Pb}$ activity, the supported $^{210}\text{Pb}$ activity has to be subtracted from the total activity. Usually a mean supported $^{210}\text{Pb}$ activity is obtained from samples with an age of more than 100 years. But often the supported $^{210}\text{Pb}$ activity varies from sample to sample. Then, there is need to determine the supported $^{210}\text{Pb}$ value from $^{226}\text{Ra}$ measurements directly.

This paper compares the validity of these techniques. It also illustrates the applicability of the different methods by an analysis of the excess $^{210}\text{Pb}$ (i.e. total $^{210}\text{Pb}$ in the sediment less that supported by $^{226}\text{Ra}$) in lake Zurich sediments. We also discuss several techniques for the determination of supported $^{210}\text{Pb}$ (i.e., $^{226}\text{Ra}$) in lake sediments.
Experimental

Radioactivity measurements. The γ-ray intensity was measured with a well type Ge(Li)-detector. The resolution of the detector, shielded by 5 cm of pre-World War II lead, was 2.25 keV (FWHM) at 46.5 keV. The dried, powdered and weighed (1–2 g) sediment samples were sealed in glass tubes (0.9 cm diameter, 10 cm length, sample height 4 cm) and measured for about 4 days. The detector efficiency was determined with $^{210}\text{Pb}$ standard solutions of equal sample height. Betacounting of $^{210}\text{Pb}$ was carried out on a low level proportional counter (background 1.22 cpm). For α-spectroscopy we used surface barrier detectors with a resolution of 20 keV.

Radiochemical separation of $^{210}\text{Pb}$, $^{210}\text{Po}$ and $^{226}\text{Ra}$. To 0.3–0.5 g sediment samples we added $^{208}\text{Po}/^{209}\text{Po}$ tracer, lead carrier (20 mg), and barium carrier (20 mg) or $^{133}\text{Ba}$ (5 cps). The samples were digested with a mixture of 1 ml HF (40%), 3 ml HNO$_3$ (65%) and 3 ml HClO$_4$ (70%) in Teflon coated stainless steel vessels for 14 hours at 140 °C in an oven, or by a microwave technique (250W/8 min, INAUEN, personal communication). After complete dissolution, the acidic mixture was evaporated to dryness. The residue was redissolved in 25 ml of 0.75M HBr and adsorbed on a strongly anionic Dowex® 1x2, 50–100 mesh column (5 ml of resin, column diameter 1 cm). Figure 1 shows the separation scheme of the three nuclides. The method was optimized for $^{210}\text{Pb}$, because β-counting with a low level proportional counter is less sensitive than α-spectroscopy ($^{210}\text{Po}$ and $^{226}\text{Ra}$). The chemical yields were 50–75% for $^{210}\text{Po}$, 90–100% for $^{210}\text{Pb}$ and 60–85% for $^{226}\text{Ra}$.

Radium fraction (Fig. 1). The methods used for radium are based on work of GODOY, SILL and SHORT (personal communication). To the radium fraction, made up with water to 900 ml, 20 ml of concentrated H$_2$SO$_4$ and 100 ml of saturated Na$_2$SO$_4$ were added. The Ra/Ba was precipitated with 100 mg Pb$^{2+}$. In the following, the residue was centrifuged and washed with 20 ml of ethanol/water (1 : 1). The precipitation was converted to Ba(Ra)SO$_4$ or Ba(Ra)CrO$_4$ following the procedure of GODOY or converted to a colloidal suspension (SILL and LIM et al.) and separated on a 0.1 μm fluoropolymer membrane filter. The radium samples were measured 20 to 30 days after separation on a low level proportional counter. Because self-absorption in the Ba(Ra)CrO$_4$ precipitate cannot be neglected, also the dependence of the efficiency as a function of sample weight was determined by measuring $^{226}\text{Ra}$ standard sources in a similar weight range. The filtered colloidal samples were, in addition, measured by α-spectroscopy. The chemical yield was determined gravimetrically by weighing the Ba(Ra)SO$_4$, Ba(Ra)CrO$_4$ sources or by measuring the $^{133}\text{Ba}$ activity added in the colloidal technique.

$^{210}\text{Pb}$ fraction (Fig. 1). The 2M HNO$_3$ solution from the column separation was evaporated to dryness. The residue was redissolved with 1 ml 2M HNO$_3$ and diluted to