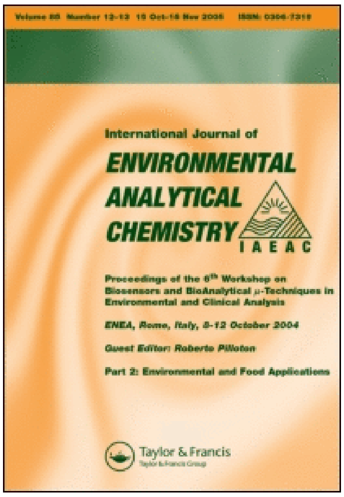

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THE PREPARATION OF CARRIER-FREE RADIUM-228 USING CATION EXCHANGE COLUMNS

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The need for a radium tracer of reasonable half-life, low cost and ready availability, led us to the preparation of carrier-free radium-228 from thorium nitrate known not to have been separated from its daughter products for at least 12 years. Solvent extraction and cation exchange techniques were used. The preparation is rapid and the characterisation of the end product by radiometric methods is straightforward.

KEY WORDS: Radium, radiotracer, cation exchange, thorium, solvent extraction.

INTRODUCTION

Uranium-238 and its decay daughter radium-226 occur together in uranium ores. Unlike the sulphate compounds of uranium, radium sulphate is essentially insoluble.[1] Consequently, the uranium is leached effectively during the milling process, but the radium deposits over the finely ground gangue solids (e.g. quartz or mica fragments) and the entire radium content of the uranium ore ends up in the solid mill wastes (the mill tailings).[2] Radium contained in the tailings is likely to be slowly leached from these solids and to enter the biosphere. Because of the long half-life of radium-226 ($\approx 1620\,a$), the mill tailings need to be managed even after the closure of a mill. The presence of radium in these materials and the amount of material produced makes alternative methods of disposal (e.g., mine backfilling or deep burial in geologically stable vaults) impractical.

Snodgrass *et al.*[3] have hypothesised that the following steps are involved in the leaching tank processes. Proton attack on the uranium and thorium minerals liberates the parent and daughter radionuclides into solution. Proton attack also liberates stable lead from the ^{238}U mineral along with barium, strontium and calcium from other minerals containing them in trace amounts. If conditions are appropriate, the metal ions and/or sulfate ion will adsorb onto a surface such as silica. If the local geometry (of the order of a few square Ångstroms) is suitable, crystal growth will be initiated. Previous work reported by us[4,5] demonstrated that such growth of hetero-epitaxial deposits of lead, barium and (barium/lead) sulfates on mica and quartz does occur. The continuation of our investigations requires the use of a radium tracer to follow radium exchange and adsorption kinetics at the surface of these deposits and for this purpose we prepared radium-228. The procedure we followed may be of use to other researchers.

EXPERIMENTAL

During the entire procedure the 1977 Recommendations of the International Commission on Radiological Protection were followed with respect to working conditions and radiation exposure. All reagents and water used were of analytical quality.

A mass of 100 g of thorium nitrate was taken from a sample known not to have been separated from its daughter products for at least 12 years. This period, in excess of 2 half-life intervals for radium-228, ensured that the quantity of radium-228 approached the maximum possible. The mass of thorium nitrate was dissolved in 200 mL of 8 M nitric acid and the resulting solution was extracted six times over a period of 20 min with 100 mL aliquots of a 40% (v/v) solution of tri-butyl phosphate (TBP) in benzene. After the sixth extraction, the aqueous phase was washed twice with 200 mL portions of dry benzene (taking the usual precautions when using this carcinogenic solvent) in order to remove residual TBP and it was then evaporated to dryness in a round-bottom flask. The procedure that we used up to this point was based on work described in reference 6. The description of the preparation of radium-228 found in this reference, while useful as a starting point does not lend itself to the routine preparation of this radio-isotope. We then used the following procedure. The residue was treated with a small volume of equal amounts of 71% perchloric acid and concentrated nitric acid, in order to destroy any remaining organic material, and this was evaporated to dryness. The dry residue was dissolved in 70 mL of 0.5 M ammonium lactate. This solution was then passed through a 50–100 mesh cation exchange column (2 cm in diameter and 20 cm in length) of Dowex 50W-X8. This was carried out at reduced pressure using the apparatus shown in Figure 1. The column was then washed with 50 mL of 0.7 M ammonium lactate, using a flow rate of 10 mL min^{-1}, to remove any rare earth cations originally present in the thorium. The column was then washed with 750 mL (approximately 50 column volumes) of distilled, demineralized water. Toward the end of this washing procedure small volumes of the eluate were evaporated to dryness on a hot plate in order to test for the presence of lactate. The radium-228 was washed from the column with 200 mL of 3 M nitric acid, using a flow rate of 10 mL min^{-1}. The solution was then evaporated to dryness in a small Pyrex beaker. A small amount of white residue was destroyed by boiling with freshly-prepared aqua regia. Upon evaporating no obvious material remained in the beaker, but intense radioactivity was found to be present when a survey

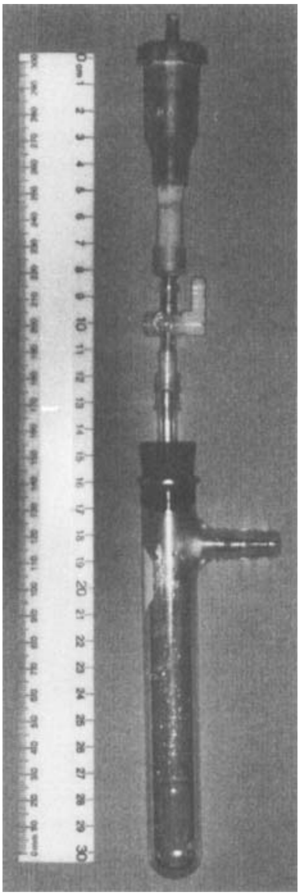

Figure 1 Apparatus used to pass solution through columns at reduced pressure.

radiation detector was placed at the mouth of the beaker. The trace of material in the beaker was taken up in 1.0 mL of 0.5 M HCl (two 0.5 mL portions) and stored in snap-top polyethylene vials. Based on data in McKay[7] and a value of 272.7 Ci/g for the specific activity of radium-228[8] we would expect a maximum yield of radium-228 of 5 μCi/100 g of crystalline thorium nitrate.

A 3-cm column of Dowex 50W-X12 was then used to separate out ^{212}Bi and ^{212}Pb (peaks A and B in Figure 2) followed by ^{228}Ac (peak C), daughters of ^{232}Th. Ammonium lactate (0.7 M) was the eluant. Samples of equal volume (10 drops) were deposited onto aluminium planchets at intervals of 30 sec, evaporated to dryness and counted in order to obtain the data for Figure 2. All counting was performed using a Mullard MX168 thin end window G.M. tube operating at a plateau voltage of 420 V, and a Griffin Timer/Scaler unit. The column was then washed with 150 mL (approximately 50 column volumes) of distilled, demineralized water to remove lactate from the column. The ^{228}Ra was then stripped from the column using 3 M nitric acid and the solution evaporated to dryness in a small Teflon beaker. Any trace of lactate residue which appeared was destroyed using

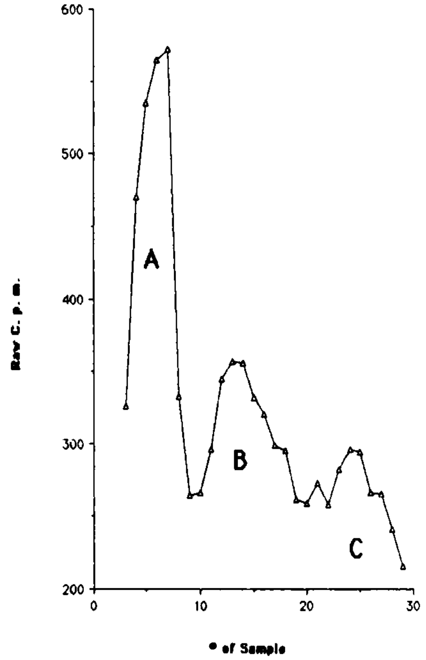

Figure 2 Plot of activity of eluate from final column, as a function of sample number. Samples collected at 30 sec intervals.

freshly prepared aqua regia and then the trace of radium-228 was taken up in 1 mL of 0.5 M HCl and stored in a snap-top plastic vial.

DISCUSSION

During the preparation of the radium-228 it became clear that the brief procedure given in reference 6 required considerable modification in order to be used as a routine method for the preparation. The quantities of ammonium lactate required in order to separate the radium-228 on a preparative scale must be removed by extensive washing of the columns before removal of the radium-228. Even the most careful washing, verified by the evaporation of test portions of the wash liquid, may leave small quantities of organic material that requires removal with freshly prepared aqua regia or perchloric acid and concentrated nitric acid. The application of reduced pressure using the apparatus shown in Figure 1 greatly reduces the time required for the separation.

Gamma-ray spectroscopic analysis of a sample prepared using our procedure was carried out using an intrinsic germanium detector and a multi-channel analyser (Canberra System 90). The resulting data are shown in Table 1. The performance of the final separation using the 3 cm column was verified by the radiometric identification of the separated components labelled A, B and C in

Table 1 Selected peaks from the gamma ray spectrum of the eluent (Canberra Series 90 system with intrinsic Ge detector)

Peak/FWHM (keV)	*Identity*
238.4 1.14	^{212}Pb
277.3 1.31	^{208}Tl
327.9 1.22	^{228}Ac
860.6 1.55	^{208}Tl
911.2 1.55	^{228}Ac

^{228}Ra gamma peaks are <31 keV and consequently were not observable.

Table 2 Regression equations for the radioactive decay constants of the daughter products of radium-228

Isotope	*Regression equation*	*Correlation coefficient*
^{228}Ac	ln net counts = 7.1236 − 0.0018 time	1.00
^{212}Pb	ln net counts = 7.0186 − 0.001 time	0.99
^{212}Bi	ln net counts = 6.5959 − 0.0108 time	1.00

Table 3 Comparison of experimental and literature half-life for the daughter products of radium-228

Isotope	*Experimental half-life*	*Literature value*	*% Error*
^{228}Ac	6.42 h	6.13 h	4.7
^{212}Pb	9.89 h	10.6 h	6.7
^{212}Bi	1.07 h	1.01 h	6.0

Figure 2, using their half-life. In the case of radium-228, an extremely soft β^- emitter, the method used to verify the identity of the nuclide once it was removed from the column was the observation of the rate of ingrowth of the actinium-228 daughter. The results of these investigations are presented in the form of the accompanying regression equations in Table 2. The coefficients of the regression equations represent the radioactive decay constants λ for the appropriate isotope and enable the half-life of the isotope to be calculated using equation (1):

$$T_{1/2} = \ln 2/\lambda = 0.6931/\text{coefficient of the regression equation.} \qquad (1)$$

A comparison of the experimental and literature values for the half-life of each of the resolved components of the decay series is presented in Table 3 and confirms the success of the separation.

As 16 hours had elapsed between the initial preparation and the gamma-ray spectroscopic examination of the radium-228, we expected to find extensive ingrowth of actinium-228 ($T_{1/2} = 6.13$ h) and traces of other thorium-232 progeny. From a perusal of the decay scheme of thorium-232,[9] the accompanying listing of gamma-ray energies obtained from the spectroscopic examination (Table 1), and tabulated gamma energies of the nuclides,[10] we were able to assign all the peaks. The results of this assignment are summarized in column 2 of Table 1 and confirm the identity of the prepared radium-228.

Our experience with this preparation suggests that it may be of use to other researchers who have need of a radium tracer.

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