ON THE INTERFERENCE OF $^{210}$Pb IN THE DETERMINATION OF $^{90}$Sr USING A STRONTIUM SPECIFIC RESIN

by

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We investigated the interference of radiolead in the isolation of radiostrontium using a strontium-specific resin by means of $^{90}$Sr and $^{212}$Pb radiotracers. The resin was found to be almost equally specific for lead ions as well. Elution of Pb$^{2+}$, however, was found to occur at very low acid concentrations ($\leq 0.02$ M HNO$_3$) of the eluant. Even with pure distilled water as the eluant, elution of lead cannot compete with strontium, due to the delayed elution dynamics caused by residual acid in the column. In contrast to strontium, which is eluted quickly from the column and almost quantitatively after 4 mL eluant (practically independently of the acid concentration of the eluant), lead is eluted with much delay and not completely after the 10 mL elution. The Eichrom method for the determination of radiostrontium in water proposes elution with 0.05 M HNO$_3$, which was found extremely useful, because at such an acid concentration, no radiolead is eluted from the column and allows the production of a pure radiostrontium fraction which can be measured by liquid scintillation counting.

Key words: radiotracer, radiostrontium, radiolead, extraction chromatography, liquid scintillation counting, environmental analysis

INTRODUCTION

Following the Fukushima nuclear accident, enormous efforts have been undertaken to monitor the released radionuclides, both in Japan [1, 2] and globally [3]. In most cases, $\gamma$-emitting radionuclides such as $^{131}$I, $^{129m}$Te, $^{134}$Cs, $^{136}$Cs, $^{137}$Cs, and others were monitored and investigated, see e.g. [4-8]. Gamma-emitters offer the advantage of allowing the qualitative and quantitative determination of the activity in a straightforward radioanalytical measurement, without major requirements with respect to sample preparation.

The analysis of other radionuclides, in particular pure $\beta^+$-emitters, is much more elaborate because it usually requires the separation of the targeted radionuclide from other $\beta^+$-emitters, which may even occur in excess. In particular, this refers to the radiostrontium isotopes $^{89}$Sr ($T_{1/2} = 50.5$ d) and $^{90}$Sr ($T_{1/2} = 28.9$ years). Both radionuclides, of which the long-lived $^{90}$Sr is regarded as the more important one, are prominent fission products and biologically relevant. Due to its chemical similarity with calcium, radiostrontium is taken up into the bone and generally believed to have a long biological half-life. Strontium-90 (maximum $\beta^+$ energy 0.5 MeV) has a short-lived daughter, $^{90}$Y ($T_{1/2} = 64$ h), which is a very poor $\gamma$-emitter as well, but a powerful $\beta^+$-emitter with a maximum $\beta^+$-energy of 2.3 MeV. Bone-seeking radiostrontium adversely affects the bone and the bone marrow and may cause leukemia [9] or skeletal malignancies [10], thus giving rise to the need of its monitoring (especially in food) after nuclear accidents [11-14]. Following the Fukushima accident, only few studies were conducted with respect to the monitoring of $^{90}$Sr [11, 15].

Environmental analysis of $^{90}$Sr (and its daughter nuclide $^{90}$Y) requires the effective separation from other $\gamma$-emitters before its measurement using liquid scintillation counting (LSC) or other radioanalytical methods. Without separation, in particular radionuclides are likely to cause interferences, especially since they usually occur in excess in the environment after a nuclear accident or explosion (both higher fission yield and volatility). Today, the separation using strontium-selective resins (“extraction chromatography”) has become state-of-the-art [16-20], although electrochemical separation of $^{90}$Y has also been used recently [21]. Previous publications [22-24] on the environmental monitoring of $^{90}$Sr using this method have already addressed the possible interference with $^{210}$Pb.

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A more in-depth evaluation of the interferences between lead and strontium and their elution dynamics is the topic of this study.

MATERIALS AND METHODS

The strontium-specific resin

The strontium-specific resin is based on crown-ether (4,4’(5’)-di-t-butycyclohexano-18-crown-6) and was purchased from Eichrom®/TrisKem® (SR-resin™) 100-150 μm. This type of resin is very selective for strontium and shows little affinity for the chemically related calcium or other typical fission products such as radionuclides. However, previous studies demonstrated a high selectivity for certain other elements, including barium, lead and polonium [25–27]. The interference with ubiquitously naturally occurring radionuclide products such as radium or actinides such as thorium. Moreover, some chemical similarity. In the environment, both elements usually occur in a divalent state [28]. Further, they have similar ionic radii in crystals: 1.18 Å for Sr²⁺ and 1.19 Å for Pb²⁺ (both for co-ordination number 6). It does, therefore, not come as a surprise that one of these elements often occurs along with the other, for example in human and animal bone [28, 29].

Experimental set-up

In this study, we have used aqueous samples which constitute not only the simplest sample matrix, but can also be regarded as a simulation of contaminated water such as rain water.

Aliquots of the ²¹²Pb (1 mL) and ⁸⁵Sr (0.2 mL) stock solutions, as well as of the lead carrier (1 mg Pb²⁺), were compounded and adjusted with concentrated nitric acid to 8 M. The Sr specific resin was equilibrated with 8 M HNO₃ for at least 45 min before loading the column with the mixture (total volume per experiment 10 mL). The column was made up of approximately 300 mg of Sr resin. The columns were reused only once, as this has previously been confirmed not to affect the resin’s performance [22, 24]. The time of loading was noted for decay correction. After loading, the column was rinsed with 2 mL of 8 M HNO₃, followed by the Eichrom-recommended rinsing, using 5 mL of a solution of 0.05 M oxalic acid in 3 M HNO₃ [31]. The elution was performed with eluents based on nitric acid with variable concentrations. Throughout the experiments, the eluent volume was constant at 10 mL.

Activities of both ⁸⁵Sr and ²¹²Pb were determined using a HPGe γ-detector (see [32–35] for details) in calibrated geometries. This allowed for the detection of residual radionuclides in the column, as well. Measurement times were 3600 s throughout the study.

RESULTS AND DISCUSSION

Pb sensitivity of the Sr specific resin

As an initial experiment, the total elutability of both ⁸⁵Sr and ²¹²Pb with different eluents was exam-
ined in order to check for the sensitivity of the Sr specific resin for Pb under different elution conditions. In this experiment, 10 mL of the eluant with variable HNO₃ concentrations (0, 0.0001, 0.001, 0.01, 0.02, 0.03, 0.04, 0.05 M HNO₃) was investigated (see fig. 1). In the analytical method for the determination of ⁹⁰Sr in water provided by Eichrom [31], an eluant of 0.05 M is suggested. At this acid concentration, Landstetter and Wallner [24] reported a total retention of Pb in the resin. We can confirm this observation. At HNO₃ concentrations higher than 0.02 M, no ²¹²Pb was eluted in detectable amounts. Gamma-spectrometric investigation of the loading solution, as well as of the resin after elution, confirmed that Pb is retained by the resin virtually completely at a loading acid concentration of 8 M HNO₃. The elution of Pb, however, only takes place to a significant extent when using water as the eluant (approximately 53% using 10 mL of H₂O as eluant) and dramatically decreases even at low HNO₃ concentrations, as shown in fig. 1. Strontium, in contrast, is almost equally between 0 M HNO₃ (i.e. pure water) and 0.05 M HNO₃, with typical recoveries around 90%. We have found that these recoveries are somewhat lower than in an investigation of environmental samples we undertook recently. One can speculate that high Th⁴⁺ concentrations may decrease the performance of the Sr resin in this case.

**Elution dynamics of Sr and Pb**

In a second experimental series, the elution dynamics for both radionuclides from the Sr resin were investigated. Hereto, the eluant was not measured as a bulk sample, but collected milliliter-wise in polyethylene vials that were measured sequentially after the experiment using the Atominstitut's sample changer. The results of this investigation are illustrated in figs. 2 (⁸⁵Sr) and 3 (²¹²Pb).

**Figure 1.** Elutability of ⁸⁵Sr (circles) and ²¹²Pb (crosses), using variable HNO₃ concentrations with the eluant. The elutability was calculated as the activity in the eluant in % of the activity of the loaded radionuclides. Uncertainties (error bars) are due to counting statistics. Results were corrected for decay, back to the time of loading.

**Figure 2.** Elution dynamics of ⁸⁵Sr in dependence of HNO₃ concentration. Uncertainties (error bars) are due to counting statistics. Results were corrected for decay, back to the time of loading.

**Figure 3.** Elution dynamics of ²¹²Pb in dependence of HNO₃ concentration. Uncertainties (error bars) are due to counting statistics. Results were corrected for decay, back to the time of loading.

Strontium proved to elute quickly, especially at low acid concentrations (fig. 2). After 4 mL or 5 mL (of 10 mL applied), ⁸⁵Sr was eluted virtually quantitatively. The maximum activity was found in the second aliquot for all eluants measured. Elution with the TrisKem-recmended HNO₃ concentration of 0.05 M was shown to be just marginally delayed, so that, when applying 10 mL of the eluant, elution performance at this acid concentration is qual to a pure H₂O eluant.

The elution of lead, in contrast, proved to be much delayed (fig. 3). The maximum activity concentration was found in mL-aliquot No. 6 (0.0001 M HNO₃) or No. 9 (0 and 0.001 M HNO₃), respectively. It is obvious that, after elution with 10 mL, some residual ²¹²Pb is still retained in the resin (as also observed by γ-spectrometry on the resin after elution). The inte-
Effects of n-octanol

In one of their pioneer works on the interference of $^{210}$Pb in the determination of $^{90}$Sr, our colleagues from the University of Vienna proposed the separation of Pb and Sr in a two-step procedure [22]. First Pb$^{2+}$ ions are separated via a Dowex ion-exchange resin (Cl-form). In a second step, Sr$^{2+}$ ions are separated from the other cations with the help of the above mentioned strontium-specific resin. Interestingly, after loading the column with 8 M HNO$_3$, Wallova et al., somehow propose the rinsing of the column with distilled water saturated with n-octanol, followed by a rinsing with 8 M HNO$_3$ (saturated with n-octanol) for further strontium purification. Further rinsing steps include 8 M HNO$_3$ (removal of bismuth and polonium) and 3 M HNO$_3$ (removal of yttrium, radium and calcium). Finally, strontium elution with distilled water is proposed [22].

We repeated this procedure on the strontium-specific resin with two small modifications. One, we repeated the experiment not only with the $^{85}$Sr tracer, but also with the $^{210}$Pb tracer in order to investigate the behavior of Pb$^{2+}$ with the n-octanol saturated rinsing solutions. Two, we used the well-proven rinsing solution consisting of 3 M HNO$_3$ and 0.05 M oxalic acid in order to efficiently remove foreign cations. Rinsing agents H$_2$O and 8 M HNO$_3$ were allowed to stay in the mixture with n-octanol for four days prior to their use for full saturation.

We found that rinsing the column with 10 mL of distilled water saturated with n-octanol already elutes Sr quite efficiently (approx. 60% of the loaded amount) and Pb (approx. 75% of the loaded amount). This result is consistent with our previous findings (figs. 1 and 2) which suggested efficient elution for both ions at a neutral pH. The elutability of $^{212}$Pb appears to be slightly enhanced when H$_2$O saturated with n-octanol is used.

It is likely that Wallova et al. meant conditioning the column using H$_2$O saturated with n-octanol and 8 M HNO$_3$ saturated with n-octanol, because the analytical separation scheme in the same publication (fig. 1 in [22]) does not mention these “rinsing” steps. After all, Wallova et al. came up with decent results in their study (relatively high $^{90}$Sr activity concentrations in animal bone), which would not have been possible if the entire amount of $^{90}$Sr was virtually accidentally eluted from the resin in the first rinsing step.

In any case, we think it is important to report this to the radiological community so that it can exercise caution when using Wallova’s analytical protocol, which, apart from this possible confusion, we found extremely suitable and recommendable.

CONCLUSIONS

The strontium-specific resin was found to be almost equally specific for lead ions, as well. The elution of Pb$^{2+}$, however, was found to occur at very low acid concentrations (≤0.02 M HNO$_3$) of the eluant. In this respect, results of the Wallner group in Vienna (who found co-elution of $^{90}$Sr and $^{210}$Pb when using distilled water) could be confirmed [24]. Even with pure distilled water as the eluant, the elution of lead cannot compete with strontium, due to the delayed elution dynamics probably caused by the residual acid in the column. In contrast to strontium, which is eluted quickly from the column and almost quantitatively after 4 mL elution (practically independently of the acid concentration of the eluant), lead is eluted with much delay and not completely only after the 10 mL elution, due to the residual acid in the column.

The Eichrom method for the determination of radiostrontium in water proposes elution with 0.05 M HNO$_3$ [31], which was found extremely useful, because at such acid concentration no radiolead is eluted from the column.

For other resins, such as the Actinide ResinTM by Eichrom/TrisKem, it has been suggested to add the resin directly into the LSC cocktail [36]. If this is done with the strontium-specific resin – loaded with both $^{90}$Sr and $^{210}$Pb – this could be quite problematic. In such a case, both $^{90}$Sr and $^{210}$Pb contribute to the counting in the LSC through direct $\beta$-radiation from the resin into the LSC cocktail and probably also through the elution of both nuclides from the resin into the non-acidic cocktail.

We observed that the resin performance (Sr recovery) was slightly poorer when loading not only $^{85}$Sr with a stable Sr carrier, but in combination with a relatively concentrated Th$^{4+}$ solution, along with a Pb$^{2+}$ carrier, indicating an interference of the resin with excess Th$^{4+}$ ions.

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**AUTHOR CONTRIBUTIONS**

Experiments were carried out by M. Kocadag, and G. Steinhauser. All authors analyzed and discussed the results. The manuscript was written by G. Steinhauser, and the figures prepared by M. Kocadag and G. Steinhauser.

**REFERENCES**


[32] Alassnig, W., et al., Expanding the Menu for Carnivorous Plants: Uptake of Potassium, Iron and Manganese...


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О УТИЦАЈУ 210Pb НА ОДРЕЂИВАЊЕ 90Sr КОРИШЋЕЊЕМ СМОЛЕ СПЕЦИФИЧНЕ ЗА СТРОНЦИЈУМ

Истраживали смо утицај радиоактивног олова при изолацији радиоактивног стронцијума користећи смолу специфичну за стронцијум, употребом 90Sr и 210Pb радиообележача. За смолу је уочено да има скоро исте карактеристике и за јоне олова. Ипак, за елуцију је нађено да се дешава при јако ниским концентрацијама киселине елуанта (≤0.02 M HNO₃). Чак и са чистом дестилираном водом као елуантом, елуција олова не може да се пореди са елуцијом стронцијума услед кашице динамике елуције изазване заосталом киселином у колони. У односу на стронцијум, који се брзо елуира из колоне и скоро увек квантитативно после 4 mL елуанта (практично независан од концентрације киселине елуанта), олово се елуира са доста кашице и то не потпуно ни после 10 mL елуције. Eichrom метод за одређивање радиоактивног стронцијума у води предлаже елуцију са 0.05 M HNO₃, што се показало веома корисним, јер при таквој концентрацији киселине нема елуције радиоактивног олова из колоне. То омогућава производњу чистог радиоактивног стронцијума који се може мерити помоћу бројача са тачним сцинтилатором.

Кључне речи: радиообележач, радиостронцијум, олово, екстракционе хроматографије, јечми сцинтиллатор, животна средина