universität wien

Dissertation

Bestimmung von ^{90}Sr und ^{210}Pb in Rehknochen und Bodenprofilen

Verfasserin
Mag. Gabriela Wallova

angestrebter akademischer Grad

Doktor der Naturwissenschaften (Dr. rer. nat.)

Matrikelnummer:	0648081
Dissertationsgebiet (It. Studienblatt):	Chemie (A091 419)
Betreuerin:	Ao. Univ.-Prof. Dr. Mag. Gabriele Wallner

Wien, Mai 2011

universität wien

Ph.D. Thesis

Determination of ^{90}Sr and ^{210}Pb in deer bones and soil profiles

Written by
Mag. Gabriela Wallova

Submitted in part fulfillment of the requirements for the degree

Doctor of Sciences (Dr. rer. nat.)

Matriculation number:	0648081
Doctoral subject:	Chemistry (A091 419)
Supervisor:	Ao. Univ.-Prof. Dr. Mag. Gabriele Wallner

Vienna, May 2011

Dedicated to my son and my husband

“I have frequently been questioned, especially by women, of how I could reconcile family life with a scientific career. Well, it has not been easy.”

Marie Curie (1867-1934)

"I hereby declare that this submission is my own work and the best of my knowledge and belief. All literature sources used during the writing of the thesis are registered in the list of references."

.....

Acknowledgements

First of all I would like to thank to my supervisor, Ao. Univ.-Prof. Dr. Mag. Gabriele Wallner for her friendly approach, continuous help, useful advices and support during last few years.

I am deeply grateful to Ing. Norbert Kandler for his help with ICP-MS measurements. I am very indebted to Dr. Mag. Sahram Ayromlou for many enthusiastic discussions and for a help with gamma spectrometry system. I thank all of my colleagues of the working group for the friendly atmosphere and versatile help, especially Dr. Michaela Srncik for a nice time in working group.

My gratitude goes to all members of Department of Nuclear Chemistry (Comenius University - Bratislava), which gave me the basic knowledges in the field of nuclear chemistry. My special thank belong to RNDr. Michal Galamboš PhD. and to RNDr. Oľga Rosskopfová for their help, inspirational consultations, fruitful ideas and encouragement. I also want to thank to RNDr. Silvia Dulanská PhD. for the useful discussions and for supplying 3M™ Empore™ Strontium Rad Disks.

I acknowledge the help of Ing. Ivo Světlík PhD., his friendly approach and explanations of scientific problems.

These lines go to my beloved family and friends for their continuous encouragement and support during the study. Especially, I thank to my son and husband for supporting me and for making all this possible.

Abstract

The presence of large amounts of ^{90}Sr and ^{210}Pb in living organisms can lead to genetic as well as somatic changes; therefore from the radiation protection point of view it's very important to monitor them in the environment. The general purpose of this work was to find a fast, sensitive, cost-effective and reliable method for the separation and measurement of ^{90}Sr and ^{210}Pb from different sample matrices, especially from deer bones and soil samples.

Initially, a well known and already published extraction chromatographic method based on the use of Sr•Spec® resin (Eichrom Industries, Inc.) for ^{90}Sr determination was applied to bone samples. However, some ^{210}Pb interference in ^{90}Sr spectra was observed in samples with higher ^{210}Pb content. Various operations were tested in order to eliminate the ^{210}Pb interferences in beta spectra. Finally, a two-steps procedure for the separation of ^{90}Sr and ^{210}Pb in animal bones and soil samples was developed. The two-steps procedure for ^{210}Pb and ^{90}Sr determination, as well as the initial extraction chromatography method based on the use of Sr-Spec resin were successfully verified using reference samples and by re-measuring samples with well known ^{210}Pb and ^{90}Sr content. Both methods were applied to deer bone samples from Austria. Although the Sr-Spec method is much faster, the two-steps procedure is preferable, since the ^{90}Sr spectrum is free of ^{210}Pb impurities and information about the ^{210}Pb content in the sample is also available.

The ^{90}Sr and ^{210}Pb separation method development was further continued and a method utilizing 3M™ Empore™ Strontium Rad disks was applied on bone samples. The study showed that 3M™ Empore™ Strontium Rad disks present an excellent separation tool for ^{90}Sr separation from bone samples.

An additional aim of the dissertation was monitoring of the activity concentrations of anthropogenic (^{90}Sr, ^{137}Cs) and natural (^{238}U, ^{232}Th, ^{40}K, ^{210}Pb) radionuclides in soil samples from three selected regions of Austria (Carinthia, Styria and Salzburg). The activity concentrations of ^{90}Sr and ^{210}Pb in soil samples were determined using the two-steps procedure, where hydroxide and oxalate precipitations were employed. The measurements of

^{90}Sr and ^{210}Pb in soil and bone samples were done by liquid scintillation counting, while the chemical yields were determined by ICP-MS. The activity concentrations of ^{40}K, ^{238}U, ^{232}Th and ^{137}Cs in soil samples were evaluated using gamma spectrometry and compared with the values already reported by UNSCEAR compilations. It was confirmed that the pollution of environment by ^{137}Cs as well as by ^{90}Sr due to the global fallout from bomb testing and the Chernobyl accident is still detectable. A correlation between the activity concentration of ^{90}Sr and ^{137}Cs in soil samples and site altitude was found. It was further found that not only the ^{90}Sr content in studied soils increases with altitude, but the same holds true for the ^{90}Sr content in deer bones from corresponding areas. It was found that ^{90}Sr content in bones is also related to the age of animal. Additionally bone and soil samples from Slovakia were examined and compared to samples from Austria. Also the teeth of a 6-years-old child were tested for ^{90}Sr content.

For the identification of an alpha-emitter as ^{210}Po (discrimination against ^{239}Pu) in urine samples 3 short separation methods using the extractive cocktail Polex®, the Sr·Spec® resin and the 3M™ Empore™ Strontium Rad disks were developed. Only a very short handling of the sample is necessary, results are available within a few hours. These fast methods are well suited in emergency situations when measurements of incorporated activities are a prerequisite for further decisions.

Keywords: ^{90}Sr, ^{210}Pb, Liquid Scintillation Counting, Bone, Soil samples, Sr•Spec® resin, Anion exchange.

Zusammenfassung

Die Anwesenheit von größeren ^{90}Sr und ^{210}Pb Aktivitätskonzentration in lebenden Organismen kann sowohl zu genetischen als auch zu somatischen Änderungen führen; aus der Sicht des Strahlenschutzes ist daher deren Messung wichtig.

Das allgemeine Ziel dieser Arbeit war die Entwicklung einer schnellen, empfindlichen, kostengünstigen und zuverlässigen Methode für die ^{90}Sr und ^{210}Pb Abtrennung aus verschiedenen Probenmaterialien, wie besonders Rehknochen und Bodenproben und desen Messung.

Zuerst wurde eine gut bekannte extraktionschromatographische Methode basierend auf der Verwendung von Sr•Spec® Harz (Eichrom Industries, AG) für die ^{90}Sr Bestimmung in Knochenproben angewandt. Es wurde jedoch eine Überlagerung der ^{90}Sr Spektren durch ^{210}Pb beobachtet, wenn die Knochen einen erhöhten Gehalt von Blei aufwiesen. Verschiedene Verfahren wurden getestet, um diese Störung zu eliminieren. Schließlich wurde eine Zweischritt-Methode für die ^{90}Sr und ^{210}Pb Trennung in Knochen- und Bodenproben erfolgreich entwickelt. Diese Zweischritt-Methode für die ^{210}Pb und ^{90}Sr Bestimmung, wie auch die Sr-Spec Methode wurde mit einer Referenzprobe und mit einer Probe mit bereits bekanntem ^{210}Pb und ^{90}Sr Gehalt überprüft. Beide Methoden wurden für Rehknochenproben aus Österreich angewandt. Obwohl die Sr-Spec Methode viel schneller ist, wird die Zweischritt-Methode bevorzugt, da das ^{90}Sr Spektrum frei von ^{210}Pb Verunreinigungen ist und der ^{210}Pb Gehalt ebenso bestimmt werden kann.

Weiters wurde eine Methode unter Verwendung von 3M™ Empore™ Strontium Rad Disks für Konochenproben erfolgreich getestet.

Ein Ziel der Dissertation war die Messung von Aktivitätskonzentrationen anthropogener (^{90}Sr, ^{137}Cs) und natürlicher (^{238}U, ^{232}Th, ^{40}K, ^{210}Pb) Radionuklide in Bodenproben aus drei ausgewählten Regionen Österreichs (Kärnten, Steiermark und Salzburg).

Die ^{90}Sr und ^{210}Pb Aktivitätskonzentration in Bodenproben wurden wieder mittels einer Zweischritt-Methode bestimmt, wo bei eine Hydroxid- und Oxalat-Fällung zum Einsatz kam. Die Messung erfolgte mittels LSC, die chemische

Ausbeute wurde mittels ICP-MS bestimmt. Die Aktivitätskonzentrationen von ^{40}K, ^{238}U, ^{232}Th und ^{137}Cs in Bodenproben wurden mittels Gammaspektroskopie ausgewertet und mit UNSCEAR Daten verglichen. Die Boden-Kontamination durch ^{137}Cs und ^{90}Sr verursacht durch den globalen radioaktiven Fallout nach den Kernwaffenversuchen und durch den Unfall von Chernobyl ist noch immer messbar. Es wurde eine Korrelation zwischen der ^{90}Sr und ^{137}Cs Aktivitätskonzentration in Bodenproben und der Seehöhe festgestellt. Dasselbe gilt auch für den ^{90}Sr Gehalt in Rehknochen. Der ^{90}Sr Gehalt hängt auch vom Alter des untersuchten Tieres ab. Weiters wurden auch Knochen- und Bodenproben aus der Slowakei untersucht, sowie die Zähne eines sechsjährigen Buben.

Für die Identifizierung eines Alpha-Emitters in Harnproben als ^{210}Po (Diskriminierung gegenüber ^{239}Pu) wurden drei kurze Trennverfahren unter Verwendung von Extraktionscoctail Polex®, Sr·Spec® Harz und 3M™ Empore™ Strontium Rad Disks entwickelt. Die Trennoperationen sind einfach und schnell, die Ergebnisse sind nach einigen Stunden verfügbar. Diese schnellen Methoden sind auch geeignet für Notfallsituationen, wenn die Messungen inkorporierter Aktivitäten Entscheidungsgrundlage für weitere Maßnahmen sind.

Schlüsselwörter: ^{90}Sr, ^{210}Pb, Flüssigsszintillationszählung, Knochen, Bodenproben, Sr•Spec® Harz, Anionenaustauscher

Table of contents

1 Introduction 1
1.1 Objectives of the thesis 3
1.2 Radioactivity of the environment 4
1.2.1 Anthropogenic radionuclides 4
1.2.1.1 Strontium 5
1.2.1.1.1 General characteristics of strontium 5
1.2.1.1.2 Separation methods for determination of ^{90}Sr 7
1.2.1.1.2.1 Selective precipitations 8
1.2.1.1.2.2 Liquid-liquid extraction (LLE) 9
1.2.1.1.2.3 Ion exchange chromatography (IEC) 12
1.2.1.1.2.4 Extraction chromatography (EC) 12
1.2.1.1.2.5 Comparison of three different separation procedures for Sr determination 20
1.2.1.2 Caesium 21
1.2.2 Natural radionuclides 22
1.2.2.1 Lead-210 22
1.2.2.2 Polonium-210 23
1.3 Measuring techniques used in this thesis 24
1.3.1 Liquid scintillation spectrometry 24
1.3.2 Germanium gamma-ray detectors 26
1.3.3 Inductively coupled plasma mass spectrometry (ICP-MS) 27
1.4 References 28
2 Results 39
2.1 Isolation and measurement of strontium-90 and lad-210 in environmental samples using a strontium-specific resin and liquid scintillation counting 43
2.2 Determination of ^{90}Sr and ^{210}Pb in deer bone samples by liquid scintillation counting after ion-exchange procedures 51
2.3 Monitoring of radionuclides in soil and bone samples from Austria 57
2.3.1 Supplementary investigations 81
2.4 Fast determination of Po-210 in urine by LSC as a means to estimate deliberate poisioning 87
3 Conclusion 99
4 CURRICULUM VITAE 105

1 Introduction

As a consequence of nuclear weapon tests in 1950 - 1963 and again after the nuclear power plant accident at Chernobyl in 1986 the determination of anthropogenic radionuclides, as e.g. ^{90}Sr has been of widespread interest. ^{90}Sr is one of the most hazardous fission products due to its chemical similarity with calcium and its following high transfer rate to the skeleton. Its accumulation to bone tissue and the high energy beta particles from its daughter nuclide ^{90}Y may cause damages to bone marrow. The ^{90}Sr activity concentrations are often measured to estimate the level of radioactive contamination in the environment, in soil, plants and living organisms to follow the migration, uptake processes and transfer factors, and to estimate the dose impact to man [1].

Dominating radiation exposure occurs through ingestion and inhalation of naturally occurring radionuclides, such as radon and its daughter products. The uptake of the primordial radionuclides remains relatively constant throughout the life [2]. ^{210}Pb is a naturally occurring radionuclide, a member of ^{238}U decay chain. Its activity concentration depends on geological composition of environment. ^{210}Pb can enter the human body through inhalation or ingestion. It has an important role in human radiation exposure as it decays to the alpha-emitter ^{210}Po. It also incorporates into bones and replaces calcium within the matrix in a manner similar to the alkaline earth metals, deposits in the skeleton long enough and thus contributes highly to the skeletal dose. When evaluating the impact of the anthropogenic ^{90}Sr, a comparison of the ^{90}Sr values with those of the natural radionuclide ^{210}Pb is reasonable and may be heplful. The presence of large amounts of ^{90}Sr and ^{210}Pb in living organisms can lead to genetic as well as somatic changes; therefore from the radiation point of view it’s very important to monitor them in the environment [2-5].

Several authors investigated the activity concentrations of ^{90}Sr and ^{210}Pb in soil and bone samples and a relationship between activity concentrations and site altitude has been studied [6,7,8,9,10]. Numerous procedures like selective precipitations, liquid-liquid extraction, extraction chromatography and ion exchange chromatography were described for ^{90}Sr or ^{210}Pb determination in varous matrices. In many cases the procedures for ^{90}Sr determination are tedious and time consuming, coupled with production of huge amounts of waste, or lack separation efficiency due to the mutual cross-contamination by lead and other interferents. The complexity of some procedures and their reliance on ^{90}Y ingrowth make these methods unsuitable for the use in emergency situations. The main objective of the study was to develop a fast, cheap and reliable method for separation and measurement of ^{90}Sr and ^{210}Pb in soil and bone samples.

The bones of deer are often used as “biomonitors” of possible ^{90}Sr and ^{210}Pb contamination. As deer are members of a complicated food chain, they were chosen for this research together with soil samples. The animals whose bones were used in this work were hunted to keep the equilibrium in nature and not for research interests.

In general, the radiochemical analyses of ^{90}Sr are time-consuming. Therefore in Austria the ^{90}Sr data from field studies after the Chernobyl fallout are scarce and limited to lowland areas and are missing in the range between 500 – 1700 m site altitudes [9]. This work aspires to supplement these missing data. The objective of this work was to separate and measure ^{90}Sr and ^{210}Pb in soil and bone samples from the same regions to get a better understanding of the availability of ^{90}Sr to deer. From soil data the amount of deposited ^{90}Sr can be derived directly. A drawback, however, may be rather large small-scale variations of the deposition. These variations are smoothed in the animal bones, because deer feed larger areas.

On 1st of November 2006 Mr. Alexander Litvinenko was fatally poisoned by ^{210}Po and that resulted in his death on 23th November. At the time of

Litvinenko's death, no one was quite certain what had killed him. Thallium or some unspecified cocktail of drugs had all been suggested with varying degrees of authority. Just after his death on the 24th November 2006 it was confirmed that ^{210}Po had been detected in Litvinenko's urine. The traces of ^{210}Po were found also at his home and at a London restaurant and hotel he visited the day he became ill [11]. As ^{210}Po can be determined by using tools developed for ^{90}Sr-measurements, some very fast procedures useful also in emergency situations were investigated.

1.1 Objectives of the thesis

In general, the aims of the presented thesis can be summarized in the following points:

1. Development of effective methods for ^{90}Sr and ^{210}Pb determination in soil and bone samples.
   - Verification of the methods using reference materials.
   - Comparison of the methods with already known methods.

2. Examination of soil samples for major contributors of the natural radioactivity (^{238}U, ^{232}Th and ^{40}K) and for the anthropogenic ^{137}Cs and ^{90}Sr.

3. Comparison of ^{90}Sr and ^{137}Cs content in soil profiles; study the correlation between the activity concentration of ^{90}Sr and ^{137}Cs in soil samples and site altitude.

4. Calculation of ^{90}Sr/^{137}Cs isotopic ratios in appropriate soil layers to estimate Chernobyl or global fallout impact.
5. Examination of bone samples for ^{90}Sr and ^{210}Pb content.

6. Comparison of ^{90}Sr and ^{210}Pb content in bones of deer to the content in respective soil samples. Study the soil to bone transfer factors for ^{90}Sr and ^{210}Pb.

7. Study the influence of site altitude and age of the animal on ^{90}Sr content in bones of deer.

8. Development of new methods for fast identification of an alpha-emitter ^{210}Po in urine samples for emergency situations.

1.2 Radioactivity of the environment

Ionizing radiation as well as radionuclides are inseparable from our lives. Natural radioactivity is spread in environment and comes mainly from the activity of the primordial ^{232}Th and ^{238}U and their daughters and from the activity of ^{40}K. Practically all compounds of environment such as soil, rocks, plants, air and water contain radionuclides. They are incorporated in our bodies, are present in Earth's crust, in walls of our homes, schools, offices, in our food and water. We breathe the air which contains radioactive particles. The cosmic radiation is bombarding Earth's atmosphere creating cosmogenic radionuclides. The sources of radiation can also be artificial, created by human activity. These anthropogenic radionuclides were mainly released to the environment after nuclear weapons tests and nuclear accidents like Chernobyl (1986) [12].

1.2.1 Anthropogenic radionuclides

Anthropogenic (man-made) radionuclides were created by human activities. In the second half of the 20th century the background from the anthropogenic radionuclides started to increase due to nuclear weapon tests, nuclear accidents, mining and milling operations of uranium ores, nuclear fuel fabrication processes, reprocessing of spent fuel, operations of nuclear reactors, nuclear medicine, and from storage of nuclear wastes. Significant

amounts of radionuclides were released into the environment from nuclear bomb tests and after accidents such as explosion in a high level waste storage tank at Kyshtym, former USSR (1957); accidents at Windscale, UK (1957); Three Mile Island, USA (1979); Chernobyl, USSR (1986). The Chernobyl accident was the most serious accident and has a special place in the history of nuclear reactor operations but other “smaller” releases have also importance in raising of the local radiation background [13, 14]. The typical examples of long-lived anthropogenic radionuclides released to the environment are: ^{90}Sr, ^{134}Cs, ^{137}Cs, ^{85}Kr, ^{95}Zr, ^{239}Pu, ^{129}I etc. The radionuclides can be transported into the human body through inhalation, as well as through the food chain. The United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) estimate that the average annual dose of radiation per person during the year 2000 corresponded to:

natural background: 2.5 mSv
medical diagnostics: 0.4 mSv
nuclear weapon tests: 0.005 mSv
Chernobyl accident: 0.002 mSv
nuclear fuel cycle: 0.0002 mSv

The biological as well as geochemical behavior of radionuclides must be monitored to assess the potential health risk for public. The nuclides with longer physical half-lifes, such as ^{90}Sr and ^{137}Cs have also considerable biological half-lifes and therefore are significantly harmful to humans [15,16].

1.2.1.1 Strontium

1.2.1.1.1 General characteristics of strontium

Strontium exists in nature in four stable isotopes ^{84}Sr, ^{86}Sr, ^{87}Sr and ^{88}Sr. Sr and Ca are members of the alkaline earth metals, with similar properties of cation chemistry (ionic radius, charge-to-size ratio and high coordination number). Strontium is a soft, reactive metal, first recognized in 1790 by A. Crawford. It is naturally occurring in minerals Strontianite ($SrCO_3$) and Celestine ($SrSO_4$). Strontium was named after Strontian, a village in

Scotland where the mineral was found. Strontium forms divalent cations, forms many insoluble compounds and stable chelate complexes [17].

Unstable Sr isotopes are produced at relatively high yields in nuclear fission. In the series of mass numbers 73 - 105, there are 2 radionuclides with relatively long half-lifes, i.e. ^{89}Sr, ^{90}Sr, which are pure beta emitters. Other radioactive strontium isotopes are short-lived. The title “radiostrontium“ is commonly used for ^{90}Sr and ^{89}Sr [1,12,18]. The stable and some unstable isotopes of strontium are shown in Table 1.

Isotope	Natural abundance (%)	Half-life	Decay mode	Decay energy (MeV)	Decay product
^{82}Sr	Synthetic	25.36 d	E	-	^{82}Rb
^{83}Sr	Synthetic	1.35 d	E	-	^{83}Rb
			β^+	1.23	^{83}Rb
			Γ	0.76; 0.36	
^{84}Sr	0.56			Stable	
^{85}Sr	Synthetic	64.84 d	E		^{85}Rb
			Γ	0.514D	
^{86}Sr	9.86			Stable	
^{87}Sr	7.0			Stable	
^{88}Sr	82.58			Stable	
^{89}Sr	synthetic	52.52 d	E	1.49	^{89}Rb
			β^-	0.909 D	^{89}Y
^{90}Sr	synthetic	28.8 y	β^-	0.546	^{90}Y

d – day D – delayed radiation y - years
ε – electron capture γ – gamma radiation
β^+ - positron emission β^- - negatron emission

Table 1. Stable and some unstable isotopes of strontium [18].

^{90}Sr is a pure beta emitter with a half-life of 28.8 years, decays by emission of beta particles with maximum energy of 545.9 keV to ^{90}Y and ^{90}Y to stable ^{90}Zr, Figure 1. ^{90}Y is also a pure beta emitter with a half - life of 64 hours and emits hard beta particles with maximum energy of 2.28 MeV.

$$^{90}Sr \xrightarrow{\beta,\ 0.54\ MeV,\ T_{1/2}\ =\ 28.8\ yrs} {}^{90}Y \xrightarrow{\beta,\ 2.28\ MeV,\ T_{1/2}\ =\ 64\ hrs} {}^{90}Zr,\ stab.$$

Figure 1. The scheme of radioactive decay of ^{90}Sr.

As ^{90}Sr is chemically similar to calcium it has a high transfer rate to the skeletal system. Inside of human bones together with its daughter product ^{90}Y it leads to internal irradiation which can cause bone cancer, cancer of soft tissues, leukaemia etc. ^{90}Sr and ^{90}Y belong to the most hazardous fission products [12,19,20].

Practically all ^{90}Sr brought into the upper layers of atmosphere by testing of nuclear weapons (in 1950-1960) settled back to the Earth's surface up to the 1970's. The surface contamination of soil by ^{90}Sr involves the increasing of its activity concentration in vegetable products cultivated on this soil. A reliable indicator of children exposure by ^{90}Sr is milk. Milk and milk products are the main sources of calcium for human body. The vertical migration of anthropogenic radionuclides in soil is a complex process which depends on many factors (type of radionuclide, type of soil, its permeability and chemical composition, amount of rainfall, use of fertilizers etc.) Sr has significant migration ability in soil which leads to its consecutive transport to the plants and all living organisms. The retention of strontium in soil is also affected by soil diversity, especially important is the organic mould content. Hence, into the human body ^{90}Sr can be incorporated by food chain. From the radiation point of view it is very important to study ^{90}Sr behavior in environment [19].

^{89}Sr ($T_{½}$ = 53.6 days, $E_{\beta Max}$ = 1.5 MeV) is a short lived radionuclide. It is a considerable contaminant of plants surfaces directly after a nuclear accident [19].

1.2.1.1.2 Separation methods for determination of ^{90}Sr

In recent years a large variety of methods for ^{90}Sr determination in environmental, biological, as well as in nuclear waste samples were utilized. On a large scale methods are used like extraction chromatography, selective precipitation, liquid-liquid extraction, ion exchange chromatography. Eventually the separation methods are combined depending on the sample matrix [21-29]. The aim of each of these separation methods is to separate and purify the strontium, to remove the radionuclides

which may interfere with the β-spectrum of ^{90}Sr, as well as to remove other inactive interferences presented in sample. It is necessary to choose the proper separation process, with minimal operation time, waste production, health risk for operator, costs and with a maximal efficiency and repeatability of experiment.

1.2.1.1.2.1 Selective precipitations

The precipitation methods are based upon different solubility of cations in a certain solution. Main disadvantage of these methods is a yield clearly lower than 100%. The precipitation steps are time-consuming and have to be repeated several times to obtain an adequate result. The precipitation separation methods are useful to separate Sr from alkaline earth metals (e.g. Ca, Ba, Ra), from Y and other interfering elements.

Many authors used the traditional method with fuming nitric acid to separate Sr from Ca [30-37]. The method is based on the difference between solubility of strontium and calcium nitrates in concentrated nitric acid. Sr is precipitated as nitrate several times to achieve a good separation from most elements, especially from Ca [38]. A series of chromate precipitations are provided to eliminate Ba, Pb and Ra, followed by iron hydroxide precipitations to eliminate traces of Fe, Al and other fission products. Purified ^{90}Sr is allowed to stand for ingrowth of ^{90}Y. After ^{90}Sr + ^{90}Y have reached the equilibrium, ^{90}Y is precipitated and converted to the oxalate for beta measurement. The method permits the handling of large volume samples, provides good decontaminations for the majority of interferences and is selective. The main disadvantage is working with fuming nitric acid, which gives off harmful fumes, is corrosive and presents a health hazard for the operator. The method is time-consuming and destructive for laboratory equipment [39].

To substitute the use of nitric acid, a cheaper and safer method was provided using NaOH. The method utilizes the difference in solubility of Sr and Ca hydroxides for Sr separation [40-42]. Various alternative methods for Sr separation have been introduced. Potassium rhodizonate is also a suitable

agent for Sr separation from Ca. Strontium, but not calcium reacts in neutral solution with potassium rhodizonate to form a stable precipitate [43]. The co-precipitation of Y with ferric hydroxide can be used to separate Sr from Y. The oxalate, chromate, phosphate, carbonate, hydroxide precipitations are often applied to separate a bulk of interfering radionuclides. However, all these procedures require several chemical steps before final beta-counting of ^{90}Sr [26,39,44].

1.2.1.1.2.2 Liquid-liquid extraction (LLE)

LLE or solvent extraction comprises on distribution equilibrium in the system of two immiscible solvents. The element pass to the solvent in which it is more soluble. The consolidation of phase equilibrium between two immiscible solutions is a main condition. The Nernst's distribution law is describing this equilibrium. If a solute is distributed in the same molecular form between two immiscible solvents, then for constant temperature Nernst's distribution law can be expressed as:

$$K_D = \frac{c_{org}}{c_{aq}}$$

K_D: distribution coefficient
c_{org}: concentration of solute in organic phase
c_{aq}: concentration of solute in aqueous phase

The K_D value for the extracted molecule should be considerably higher than 1. Organic substances can be easily extracted to adequate organic solvents. In case of inorganic substances, it is necessary to transfer them to the form of a neutral complex compound [45].

^{90}Y can be separated by extraction with tributyl phosphate (TBP) or bis-(2-ethylhexyl) phosphoric acid (HDEHP) from acidic medium. Tributyl phosphate (TBP) is an organophosphorous

compound used in liquid-liquid extraction of tetravalent and hexavalent actinides. A 30% solution of TBP in kerosene is commonly used in solvent extraction of uranium, thorium and plutonium from spent uranium fuel rods dissolved in nitric acid in PUREX process (nuclear reprocessing process) [14]. Pure TBP is used for extraction of Y from concentrated nitric acid solution. For ^{90}Sr determination in reactor wastes extraction with TBP was repeated three times and Cerenkov radiation of the high-energy beta-particle emission of ^{90}Y was measured [46]. To determine the activity concentration of ^{90}Sr in human bones, the extraction of Y with TBP followed by Y-oxalate precipitation can be utilized [47]. In determination of ^{90}Sr in mushrooms and soil, the extraction of Y by TBP followed precipitation of Y as hydroxide from the organic phase by the addition of ethanol and ammonium hydroxide. To separate Y from Fe, two oxalate precipitations of Y were provided [48]. An improved method of ^{90}Sr determination in environmental matrices (as e.g. raw and dried milk, plants, soil) was elaborated. In this method Th radioisotopes (especially ^{234}Th) were extracted by Aliquat 336 from 8M HNO_3 before the TBP extraction. Y was precipitated as oxalate after extraction by TBP [52]. Many other extractants e.g. t-octyl phosphine oxid (TOPO) or tenoyl-tri-fluoracetone (TTA) have been used for Y extraction [49]. The method was utilized in radiochemistry laboratories to eliminate the use of fuming nitric acid method. However, all separation methods based on ^{90}Y analysis require more than 14 days to achieve radioactive equilibrium, therefore they are not suitabe in emergency situations. Moreover, the applied organic solvents (TBP, DEHPA, dichlormetane) are toxic and present a health risk for the operator [50-55].

Pedersen in 1967 reported the synthesis, metal ion complexation properties and unusual ligating properties of a large number of macrocyclic polyethers, so called crown ethers [56]. In 1987, the Nobel price in chemistry was awarded to three researchers in macrocyclic chemistry, namely C. J. Pedersen, D. J. Cram, and J.-M. Lehn.

Crown ethers are the cyclic oligomers of dioxane. The essential repeating unit of any simple crown ether is ethyleneoxy (-CH_2-CH_2O-) which repeats twice in dioxane and six times in 18-crown-6. Several crown ether structures are presented in Figure 2.

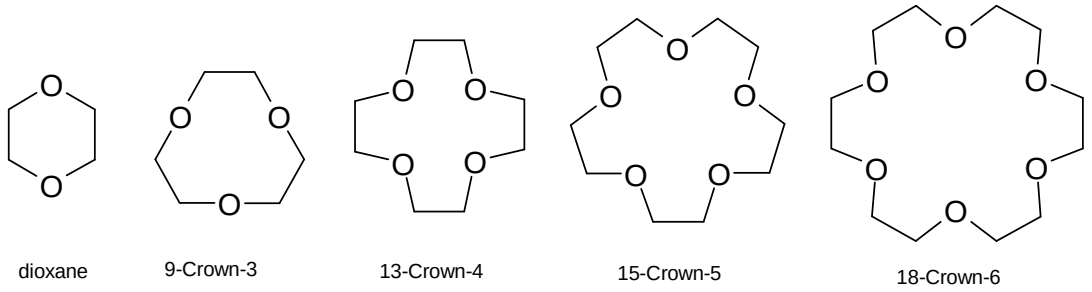


Figure 2: Cyclo-oligomers of ethylene oxide, from dioxane to 18-crown-6 [57].

Crown ethers are colorless, neutral and soluble in aromatic solvents (especially in chloroform and chloromethane). The first number in crown ether's name corresponds to the number of atoms in cycle and the second number refers to the number of oxygen atoms in cycle. Crown ethers have the ability to bind certain cations by forming complexes. The interior of the ring is hydrophilic; the oxygen atoms can coordinate with the cation situated at the interior of the ring. The oxygen atoms behave like a Lewis base because of the free electrone pair orientated to the interior of the cavity. The exterior of the ring is hydrophobic and for this reason resulting cations often form salts which are soluble in nonpolar solvents. Some of these cyclic ethers form relatively stable complexes with alkali and alkaline earth metal ions [56,57]. Since Pedersen´s discovery studies of crown ethers have grown tremendously. The use of these macrocyclic polyethers for the separation of strontium and calcium has been proposed [58-60]. After several studies, it was established, that the satisfactory separation of strontium and calcium is achieved using either dicyclohexano-18-crown-6 or dibenzo-18-crown-6 [61].

1.2.1.1.2.3 Ion exchange chromatography (IEC)

Ion exchangers are high molecular weight organic polymers (e. g. di-vinyl-benzene and styrene) containing diverse functional groups covalently bound to the polymer support. Ion exchangers are practically gel dispersed systems where the dispersed medium is a low-molecular solvent (water). The polymer skeleton can be inorganic (zirkonylphosphate, aluminosilicates) or organic (polymer exchanger, exchanger on cellulose or dextrine basis). According to the functional ability they can be divided into cation exchange resins (catexes) and anion exchange resins (anexes). The reticulated bonds (ion bonds, metylene or di-vinyl-benzene bridges) together with polymer chain create a tridimensional skeleton. The ions of the resin (e.g. $–SO_3H$, -COOH, $-NH_2$ etc.) can be exchanged by ions from solutions which flow through them.

For separation of alkaline earth ions frequently used cation exchangers are strongly acidic sulfonated resins containing $-SO_3^-$ groups. The affinity to the functional group $–SO_3H$ is decreasing in line: Ra>Ba>Sr>Ca>Mg [62].

The cation exchange behavior of Sr was investigated in a variety of samples and in different solutions of acids (e.g. HNO_3, HCl, HBr) [63-65].

1.2.1.1.2.4 Extraction chromatography (EC)

EC is also called solid state extraction (SPE). It is an extraction method where liquid extractants are sorbed on the surface of an inert solid support material (silica or resin as solid sorbents packed into disposable plastic or glass cartridges or imbedded into Teflon or glass fiber disks). A part of extraction chromatographic resin bead is depicted in Figure 3.

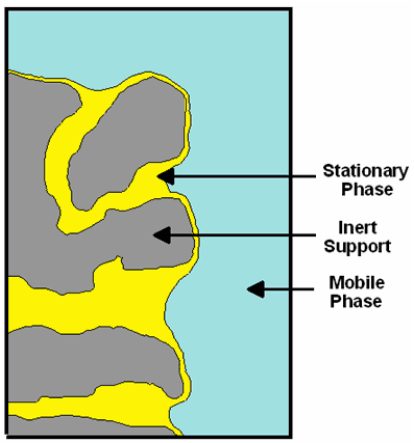


Figure 3. Surface of porous extraction chromatographic resin bead [66].

The studied analyte is dissolved in a liquid phase. Then the analyte is sorbed from liquid phase into solid phase. The interaction of the analyte with solid phase has to be stronger than its interaction with liquid phase where it is dissolved. The mobile phase is usually an acid solution, eventually complexants are used to enhance selectivities or rinsing of strongly bound metals from the column. SPE techniques were developed to substitute many traditional liquid-liquid extraction methods for strontium determination in aqueous matrix [45,66]. The process of extraction is realized in the thin surface layer providing excellent contact of the reagents. SPE techniques provide many advantages compared to ion exchange or solvent extraction. The main advantage is much less consumption of organic solvents which are usually health-hazardous and harmful for environment. The advantages of SPE compared to IEC and LLE are summarized in following points [67,68]:

- rapidity, accuracy, reproducibility
- simple procedure
- less reagents and chemicals used
- less waste solutions produced
- less glassware used
- high recoveries

- time saving

It was found, that strontium may be effectively extracted from nitric acid by a 1M solution of 4,4´(5´)-bis(tert-butylcyclohexano)-18-crown-6 (DtBuCH18C6) in 1-octanol (Figure 4) sorbed on an inert substrate.

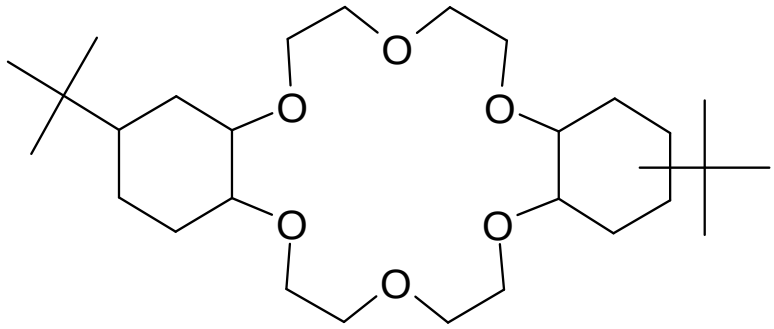


Figure 4. Structure of 4,4',(5')-bis(tert-butylcyclohexano)-18-crown-6 [68].

It has been shown that this material has sufficient selectivity to permit the isolation of strontium from samples containing diverse interfering radionuclides and also from samples containing huge amount of calcium [69-71]. Nowadays, this reagent is available commercially as Sr Resin (so called Sr▪Spec) from EiChrom Industries, Inc. and TRISKEM Int. The extraction equilibrium can be expressed as follow:

$$Sr^{2+}_{(aq)} + Crown_{(org)} + 2NO_3^- \leftrightarrow Sr(Crown)(NO_3)_{2(org)} \quad [68,70]$$

In Figure 5 is described nitric acid dependency of capacity factor k´ (the number of free column volumes to peak maximum) for alkali and alkaline earth elements at room temperature.

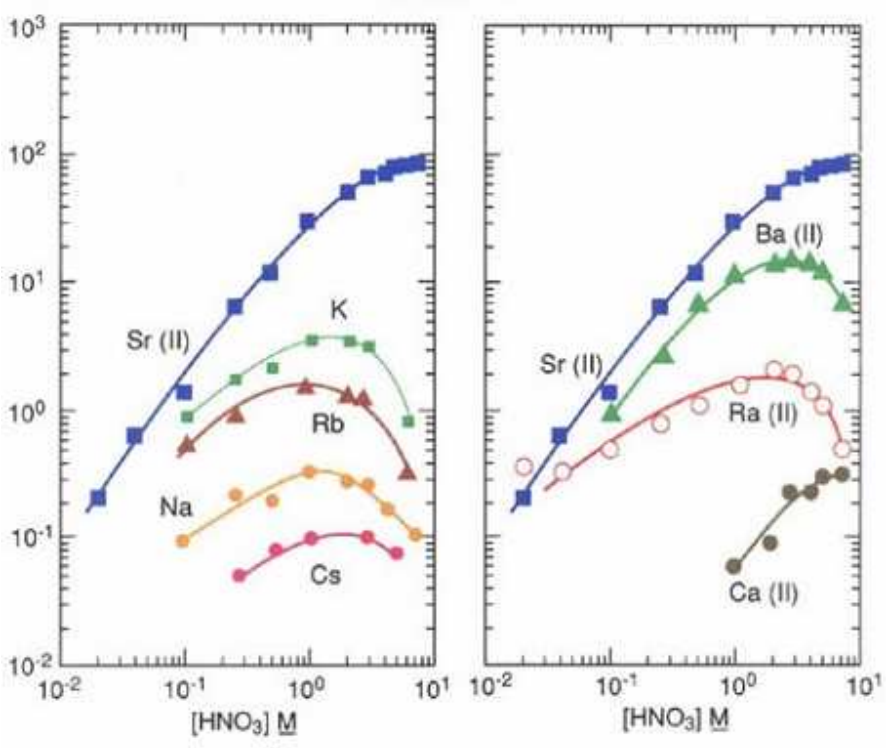


Figure 5. Dependence of the capacity factor (k´) for alkali and alkaline earth metal ions on nitric acid concentration at 23-25℃. Particle size of loaded resin: 50-100μm [71]

From Figure 5 can be seen, that sorption of strontium on Sr resin gets higher with increasing concentration of nitric acid. At 8M HNO_3 medium the sorption of strontium is most significant with a capacity factor of strontium of approximately 90; at 0.05M HNO_3 the capacity factor is lower than 1. In the whole concentration range alkali and other alkaline earth metal ions exhibit much less affinity to Sr Resin than strontium. The lowest sorption ability has calcium; it can be easily separated from strontium by rinsing the column with 3M HNO_3. Sr resin exhibits selectivity towards Sr ions with respect to several cations (i.e. Y, Zr, Na, Li, Mg, Mn, Al, Ag, Fe, Co, Cu, Ni, Zn, Cd, Ca, Ba) from 3M HNO_3 medium. From Figure 6 it can be seen, that Sr resin is selective for Sr over Ba, Ra, K. The highest sorption capacity exhibits barium which can be separated from strontium by rinsing the resin with 8M HNO_3 [71]. The elution behavior of a selection of elements on the Sr Resin is charted in Table2.

Percent of element found in F.C.V.								
3M HNO_3 – 0.01 M Oxalic acid							0.05M HNO_3	
Element	1-5	6-10	11-15	16-20	21-25	26-30	31-40	F.C.V
Li	100	-	-	-	-	-	-	
Na	100	-	-	-	-	-	-	
K	66	35	-	-	-	-	-	
Rb	100	-	-	-	-	-	-	
Cs	100	-	-	-	-	-	-	
Mg	100	-	-	-	-	-	-	
Ca	100	-	-	-	-	-	-	
Sr	-	-	-	-	-	-	99	
Ba	-	-	53	42	6	0.7	-	
Ra		99	-	-	-	-	-	
Al	100	-	-	-	-	-	-	
Cr	100	-	-	-	-	-	-	
Mn	100	-	-	-	-	-	-	
Fe	99	0.6	0.2	0.4	-	-	-	
Co	100	-	-	-	-	-	-	
Ni	100	-	-	-	-	-	-	
Cu	100	0.2	-	-	-	-	-	
Zn	100	0.2	-	-	-	-	-	
Y	100	0.1	-	-	-	-	-	
Zr	91	0.4	0.2	-	-	-	-	
Mo		84	16		-	-	-	
Tc	57	43	-	-	-	-	-	
Ru	100	-	-	-	-	-	-	
Rh	100	-	-	-	-	-	-	
Pd	100	-	-	-	-	-	-	
Ag	15	88	2	-	-	-	-	
Cd	100	0.1	-	-	-	-	-	
La-Eu	100	0.1	-	-	-	-	-	
Hg	5	5	19	40	19	10	5	

Table 2. Elution behaviour of common elements and fission products of the strontium-selective resin (Column parameters: Particle size=50-100µm, Bed volume = $1cm^3$, Bed hight = 5.0 cm, F.V.C = 0.60 mL) [71].

The capacity factor of potassium is close to 100. It may cause interferences in case of samples with large amounts of potassium (as e.g. soil samples). It was suggested to use the oxalate precipitation for Sr preconcentration and separation from alkali metals [68].

Pb is retained by this resin more strongly than Sr over the wide range of nitric acid concentrations, Figure 6.

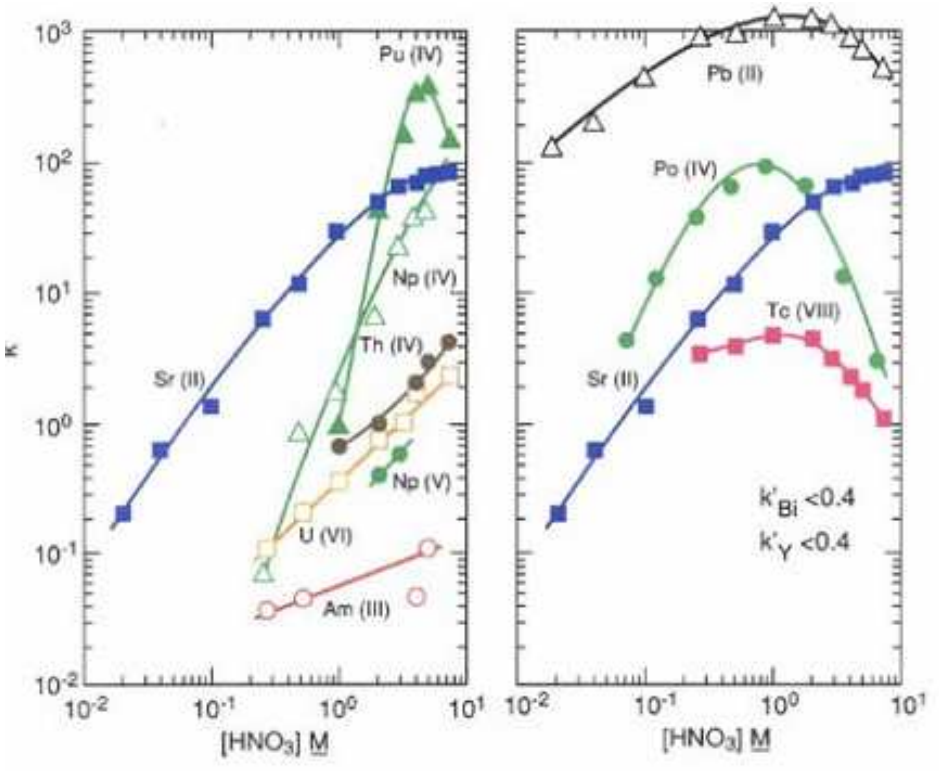


Figure 6. Dependence of the capacity factor (k´) for various ions at 23-25℃ on the nitric acid concentration. Particle size of loaded resin: 50-100μm [71].

Tetravalent neptunium, plutonium and polonium are retained at least as well as strontium over certain ranges of acidities. To prevent the retention of tetravalent actinides on Sr▪Spec Resin, addition of oxalic acid as competitive complexing agent can be utilized [71].

It was found that the maximum resin capacity for strontium is 8.1 mg of Sr per gram of Sr▪Spec Resin. Up to 2 g of calcium and 200 mg of potassium can be loaded on the Sr column (3g Sr Spec) without decrease of strontium recovery [72].

Separation of ^{90}Sr from large variety of samples like milk, urine, soil, bones, food, milk etc. was utilized using Sr▪Spec Resin. Precipitation steps are widely used before the purification of Sr on Sr▪Spec Resin to remove the bulk of interfering elements i.e. iron, potassium, alkali metals [8,25,29,68,72-76].

When determining Sr in environmental samples with higher ^{210}Pb content some authors observed impurities in beta spectra of ^{90}Sr. The obtained spectra revealed that the impurity was caused by ^{210}Pb and its

daughters ^{210}Bi and ^{210}Po. It was found that in some cases, when the ^{210}Pb in the sample is in excess to ^{90}Sr, the extraction chromatographic method based on the use of Sr resin is not sufficient to eliminate the ^{210}Pb traces (and its daughters ^{210}Bi and ^{210}Po) in the Sr fraction. To achieve better separation of Sr from Pb in bone and plants samples, lead iodide precipitation was utilized before Sr counting [77]. It was also found that in case of soil samples the practical way to avoid interference from ^{210}Pb in the ^{90}Sr spectra was to perform three precipitations before bringing the sample to the Sr Spec column. Hydroxide precipitation was utilized to remove Fe, which co-precipitates also ^{210}Pb. Addition of Pb carrier followed by chromate precipitation (Pb and Ba are quantitatively precipitated) and finally carbonate precipitatation of Sr was applied. Precipitated carbonates were dissolved in nitric acid and loaded onto Sr Spec column in 3M HNO_3 [76].

Sr Resin is often used in combined procedures for determination of Sr and actinides. In combined procedures, actinides are concentrated and removed by co-precipitation, anion exchange or extraction chromatography and Sr is removed usually by EC with Sr Resin. The main principle of these methods is that actinides are separated first before separation of Sr by Sr▪Spec Resin [78-83].

For the analysis of liquid samples (i.e. surface, ground, drinking water) a selective disk, Empore™ Strontium Rad Disk has been developed [84]. The SPE Empore™ Sr Rad Disk (3M Corporation) uses a Sr-selective crown ether extractant (AnaLig™ Molecular Recognizing Technology by IBC Advanced Technologies) mounted on polytetrafluoroethylene (PTFE) fibrils. PTFE is an inert material which has no influence on the absorption properties of sorbent. The whole separation process using Empore™ Sr Rad Disk requires only 30 minutes of operator time. The advantages of Empore™ Sr Rad Disk application can be summarized in following points [84-86]:

- high separation efficiency
- easy manipulation

- unpretending in time and technical skills
- elimination of waste
- minimalization of sample volume and volume of eluent

In the process of sorption on Empore^{TM} Sr Rad Disk the stable strontium is a competitor for radiostrontium. To obtain quantitative recovery the sum of stable and radiostrontium loaded onto the disk should not exceed 3mg (Table 3) [85,87].

Interfering cation [a]	Sr Retention, % (± 2%)	
	2M HNO_3 [b]	4M HNO_3 [b]
10.000 ppm Li^+		99
10.000 ppm NH^{4+}	6	10
10.000 ppm Na^+	76	83
10.000 ppm Mg^{2+}		97
10.000 ppm K^+	1	3
10.000 Ca^{2+}	33	24
100 ppm K^+	53	89
100 ppm Ca^{2+}	99	97
100 ppm $NH4^+$	96	97
10 ppm Pb^{2+}	22	17
1ppm Pb^{2+}	97	99
0.1 ppm Ba^{2+}	101	97
Stable strontium effect		
$[Sr^{2+}]$		4M HNO_3
1.6 mg		98
3.2 mg		97
6.4 mg		63
8.0 mg		52

[a] solutions were prepared from the chloride salts of listed cations, except for Sr solutions, prepared from nitrate salt.

[b] samples contained 1.6 mg strontium per liter of nitric acid solutions.

Table 3. Cation interference on sorption of radiostrontium by EmporeTM Sr Disk [87].

It was reported that the radiochemical yield of ^{90}Sr was greater than 70% for ground water samples and the determination results were in good agreement with those obtained with conventional methods [88]. It was found, that optimal Sr uptake on Sr Rad Disk is at ≥ 2M HNO_3. Also barium, radium and lead are retained by the Disk (Table 3) [87]. At levels typical for environmental samples these interferences are minimal. It should be avoided during the whole

filtration procedure to pass air through the filter in order to decrease possible interferences from radon daughter entrapment on the disk.

The disk is conditioned with methanol before the separation. The sample solution is acidified to 2-4M HNO_3 or HCl, followed by flowing through the disk under slight vacuum. The daughter ^{90}Y can be stripped from the disk with 2M HNO_3. It is possible to strip Sr from the disk with adequate complexing agent (as e.g. ethylenediaminetetraacetic acid - EDTA). $EDTA^{4-}$ usually binds to metal cation through its two amines and four carboxylates (Figure 7) [89]. The Empore™ Sr Rad Disks are expensive and this may be the reason, that this material is only rarely used [90-92].

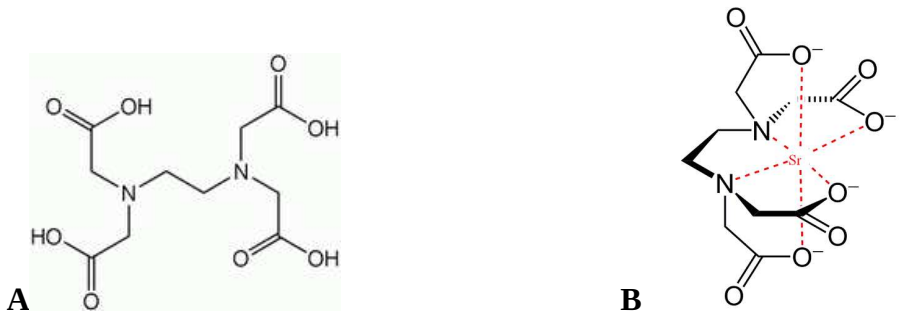


Figure 7. A) structure of ethylenediaminetetraacetic acid B) EDTA-Sr-chelate complex

1.2.1.1.2.5 Comparison of three different separation procedures for Sr determination

Three radiochemical procedures for the determination of ^{90}Sr in environmental samples (fuming nitric acid method, EC method using Sr Resin and method using ion exchangers) were compared [93]. All results obtained by the analysis of tea, rice, soil and milk by the tree methods agreed well. When using Sr▪Spec Resin the time needed is much shorter than for the other two methods. In the cited work three counters were used: a low-background counter, a liquid scintillation counter and a Cerenkov counter. Due to the low background of the liquid scintillation counter the

detection limit for Cerenkov counting is about two times higher than that for low-background counting.

Three EC materials (AnaLig Sr-01 – molecular recognizing ligand covalently bounded to inert support, produced by IBC Advanced Technologies, Sr Resin and Empore^{TM} Sr Rad Disk) were studied for Sr determination in environmental samples [94]. It was found that all studied materials are suitable for quantitative and reliable Sr separation from aqueous solutions. Slightly higher Sr recoveries were observed for the separation method with AnaLig Sr-01 and Empore^{TM} Sr Rad Disk.

1.2.1.2 Caesium

As mentioned in chapter 1.2 the significant amount of anthropogenic radionuclides like Cs radioisotopes were released to the environment due to nuclear explosions, accidents like Chernobyl, nuclear fuel cycle activities and nuclear medicine. ^{134}Cs with half-life of 2.062 years is a rather short-lived caesim isotope. Due to its short half-life, the presence of ^{134}Cs in environmental samples would indicate a very recent nuclear accident. ^{134}Cs released from Chernobyl accident and from testing of nuclear weapons decayed already below detection limit.

The most significant Cs isotope is ^{137}Cs (half-life of 30.1 years, with maximum beta energy at 0.51 MeV and 1.18 MeV; maximum gamma energy at 661.6 KeV). In environment ^{137}Cs migrates, sorbs onto natural matrices and enters to the food chain. ^{137}Cs can be transported to the human body by ingestion or inhalation of resuspended matter, it is distributed by blood thought the whole body and accumulates in soft tissues and muscles. The presence of this radio-toxic metal in human body can lead to somatic as well as genetic changes and therefore is carefully monitored in the environment [95-97].

1.2.2 Natural radionuclides

The natural radionuclides are those with lifetimes comparable to the age of earth (primordial radionuclides) or those which are components of natural decay chains beginning with ^{232}Th, ^{238}U and ^{235}U.

The main part of natural radioactivity stems from the activity of the primordial radionuclides ^{238}U and ^{232}Th together with their radioactive daughter products and from ^{40}K. The activity concentration of ^{40}K in soil is an order of magnitude higher than that of ^{238}U and ^{232}Th. More than 50% of our annual effective radiation dose comes from inhalation of the ^{238}U decay progeny ^{222}Rn and its daughters, and about 10% derives from intake of radionuclides by ingestion of food or water. Natural radionuclides are present in varying degrees in air, in water, in organic materials and in living organisms. External terrestrial radiation sources contribute by around 10% of the annual dose and are mainly caused by ^{40}K and by γ-emitting decay products of ^{238}U and ^{232}Th. There are some areas of markedly higher absorbed dose rates in air throughout the world that are associated with thorium-bearing and uranium-bearing minerals in soil. The background radiation varies from place to place depending on mineral composition of the soil [15,16]. Thus, the knowledge of the distribution of these radionuclides is of principal interest [98-101].

1.2.2.1 Lead-210

^{210}Pb is a naturally occurring radionuclide and the member of the uranium-238 decay chain. ^{210}Pb emits low energy beta particles ($E_{\beta max}$ =20keV in 81%, 61keV in 19%) and gamma rays (E_{γ}=46.5 keV in 4.06%) with a half-life of 22.3 years. It is considered as one of the most toxic natural radionuclides remaining in skeleton long enough to produce a high skeletal dose. The daughter products of ^{210}Pb are ^{210}Bi (β-emitter with a half-life of 5.012 days) and ^{210}Po (α-emitter with a half-life of 138.376 days) [102].

Several methods for ^{210}Pb determination in environmental samples (i.e. selective precipitations, solvent extractions, ion exchange) were described

[102-105]. In high activity samples ^{210}Pb can be evaluated directly using gamma spectrometry system where the gamma line at energy 46.5 keV is used. The activity of ^{210}Pb can by determined indirectly from measurement of ^{210}Po alpha particles after its ingrowth from ^{210}Pb. This method is time consuming and could not be applied for emergency samples because of time needed for the ingrowth of ^{210}Po (more than 6 months) [106]. Other indirect methods for ^{210}Pb determination are based on measuring its beta emitting daughter ^{210}Bi using low-level background alpha/beta proportional counting or liquid scintillation counting [107,108]. ^{210}Pb is of environmental importance because of its contribution to natural radiation dose [109,110].

1.2.2.2 Polonium-210

Polonium isotopes are produced via natural uranium and thorium decay and also by artificial induced nuclear reactions. Natural ^{210}Po is a member of uranium decay chain, it occures in environment after out-gassing and subsequent decay of ^{222}Rn. ^{210}Po (half-life of 138.376 days) decays directly to its stable daughter ^{206}Pb by emission of alpha particles. Due to its short half-life, ^{210}Po is extremely radiotoxic if incorporated into the human body. After ingestion or inhalation it is taken up in the blood, distributed in soft tissues, in kidney, liver, spleen and bone marrow.

It can be significantly enriched in various biological samples such as fish and shellfish [111,112]. Most of the methods involved for its determination are based on chemical separations (ion exchange, solvent extraction, extraction chromatography) and α-spectrometry measurements. Nickel, copper or silver disks are used to make polonium alpha-sources, because Po spontaneously deposits on these metals. The extractive liquid scintillation cocktail POLEX^{TM} (trioctylphosphine oxide as extractive molecule) was developed for extraction of polonium from aquous samples. POLEX^{TM} provides a fast and simple method for determination of Po isotopes from phosphoric acid solution [111-113].

1.3 Measuring techniques used in this thesis

1.3.1 Liquid scintillation spectrometry

A scintillation detector consists of a scintillator optically coupled to the photomultiplier tube, Figure 8.

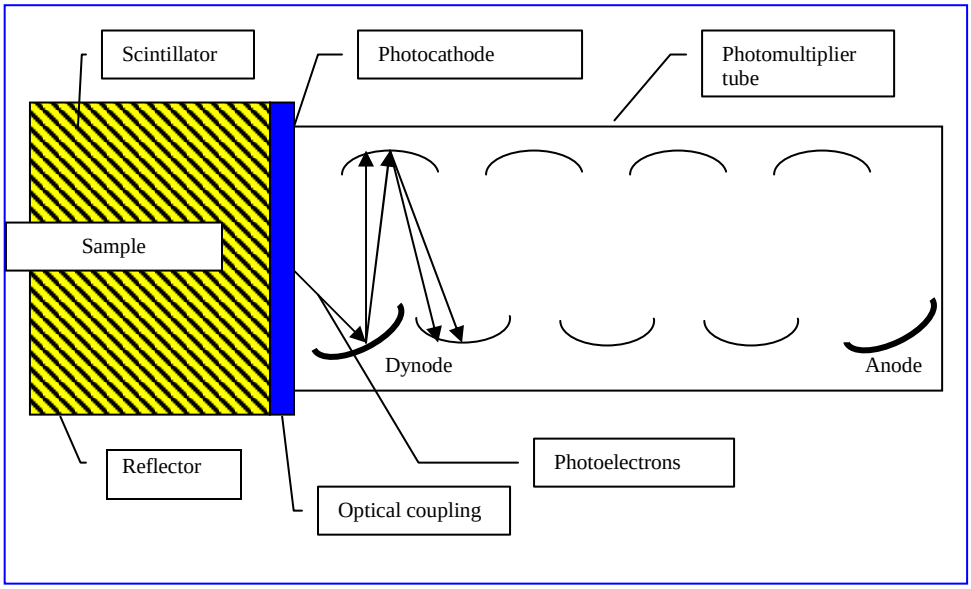


Figure 8. Scintillation detector

Ionizing radiation interacts with scintillator and produces photon flashes, which are converted to photoelectrons by a photocathode. Photoelectrons are multiplied in the electron multiplier thus giving detectable voltage pulses. A scintillating material is usually an inorganic crystal or an organic solid (for γ-detection) or an organic liquid (best suited for low-energy betas) [14]. The amplitude of the pulse is proportional to the amount of light that has reached the photomultiplier tube i.e. it is directly proportional to the energy of the emitted particle. The measuremet by LSC involves the mixture of the aquous sample with an appropriate scintillation cocktail. Scintillation vials have to be transparent at the wavelength of the used scintillator and resistant to the solvent. The liquid scintillator is prepared by dissolving of scintillation material in suitable organic solvent. The scintillation cocktail is usually composed of following components:

- solvent: toluene, xylene, benzene etc.
- scintillator: PPO (2,5-diphenyloxazole)
- wavelength shifters: POPOP (p-bis-[2-(5-phenyloxazolyl)]benzene); If the scintillator emits photons with a wavelenth too short for maximum photomultipier sensitivity it is shifted to lower vawelengths.

Several liquid scintillation cocktails are nowadays commercially available (Ultima GoldTM, HiSafe®III etc.) [111,114]. Liquid scintillation counters offer several advantages compared to other detectors especially for low energy beta counting as attenuation by the detector window, backscattering and self-absorption are avoided [14]. The main advantage of liquid scintillation counting is a high counting efficiency (90-100%) [114]. Liquid scintillation spectrometers as e.g. Quantulus®1220 low-level counter (Wallac Oy, Finland, now Perkin Elmer) provide information about the shape of spectra and enables to differentiate between α- and β-emitters by pulse shape analysis. Background is very low due to passive and active (electronic) shielding (Figure 9). Quantulus®1220 was used in this work as a reliable technique for ^{90}Sr, ^{210}Pb and ^{210}Po determination.

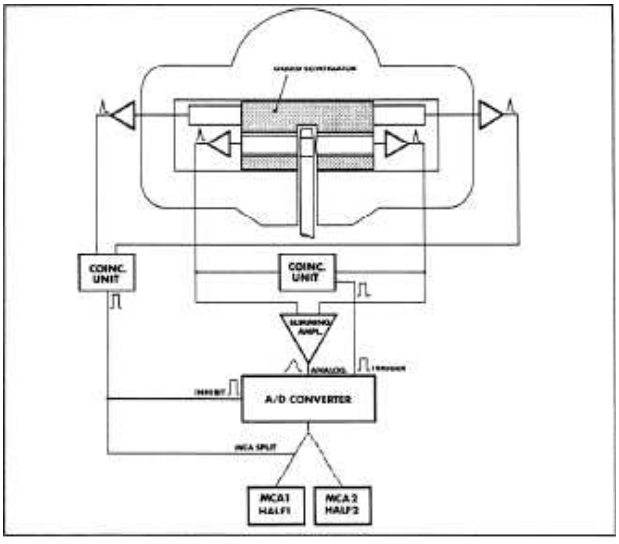


Figure 9. Outline of the liquid scintillation counter Quantus®1220, WallacOy, Finland (now Perkin-Elmer) [115].

1.3.2 Germanium gamma-ray detectors

Germanium detectors are semiconductor detectors. After interaction of photons with the sensitive area of detector, electrons and holes along the photon track are created. The created charge is proportional to energy deposited in detector and is converted into a voltage pulse by a preamplifier. The shape and amplitude of pulse is a function of detector geometry and of electric field distribution.

Reverse-Electrode Ge Detector (REGe) Canberra (GR 2020) with 20% eficiency relative to NaI and 3 keV resolution was used in this work. The geometry of the REGe detector is similar to other coaxial germanium detectors. The REGe detectors have opposite electrode configuration than coaxial detectors, P-type electrode is outside and N-type electrode is inside (Figure 10). This kind of detector is suitable for medium and high energy γ-rays detection (5 keV – 10 MeV). It was observed that radiation damages in convential coaxial detectors due to charged particles and neutrons cause hole trapping in germanium. In REGe detectors the holes are collected by the outside electrode. The detector is placed in a low-background lead shield.

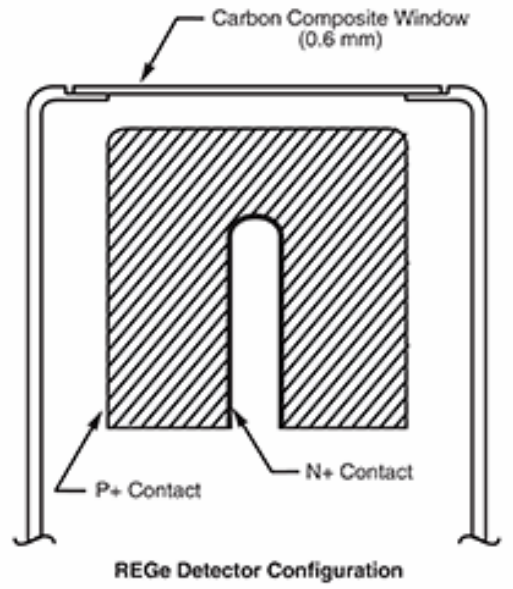


Figure 10. REGe detector cross section [116].

Because of relative low band gap of germanium these detectors have to be cooled by liquid nitrogen in order to reduce the thermal generation of charge carriers [116].

1.3.3 Inductively coupled plasma mass spectrometry (ICP-MS)

ICP technology was built upon the same principles used in atomic emission spectrometry. Nebulized aerosol of the samples is atomized and ionized in high temperature argon plasma and analyzed based on their mass to charge ratios. ICP-MS is excellent tool for measurement of the trace elements as low as one part per trillion (ppt). It is also possible to scan more than 70 elements to determine the composition of an unknown sample. A schematic diagram of the ICP-MS, 7500 Series (Agilent) instrument is shown in Figure 11 [117]. In this work chemical yields for strontium and lead separations were determined by ICP-MS Agilent 7500ce Instrument, equipped with a CETAC ASX-520 autosampler from Waldbronn, Germany.

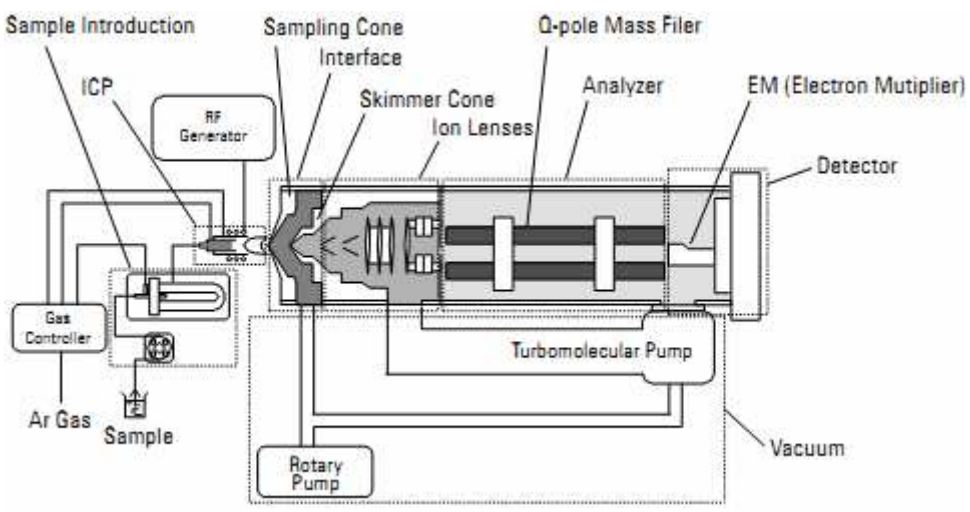


Figure 11. A schematic diagram of the ICP-MS, 7500 Series (Agilent) instrument [117].

1.4 References

[1] Vajda N, Kim CK (2010) Determination of radiostrontium isotopes: A review of analytical methodology. Appl Radiat Isot 68(12):2306-2326

[2] Swift B (1998) Dating human skeletal remains: Investigating the viability of measuring the equilibrium between ^{210}Po and ^{210}Pb as a means of estimating the post-mortem interval. Forensic Sci Int 98:119-126

[3] Grahek Z, Mcefat MR, Lulic S (2006) Isolation of lead from water samples and determination of ^{210}Pb. Anal Chim Acta 560:84-93

[4] Maxwell SL (2008) Rapid analysis of emergency urine and water samples. J Radioanal Nucl Chem 275(3): 497-502

[5] Miro M, Gomez E, Estela JM, Casas M, Cerda V (2002) Sequential injection ^{90}Sr determination in environmental samples using a wetting-film extraction method. Anal Chem 74:826-833

[6] Landstetter C, Wallner G (2006) Determination of strontium-90 in deer bones by liquid scintillation spectrometry after separation on Sr-specific ion exchange columns. J Environ Radioact 87:315-324

[7] Strandberg M, Strandgaard H (1995) ^{90}Sr in antlers and bone of Danish roe deer population. J Environ Radioact 27:65-74

[8] Asgharizadeh F, Salimi B, Ghannadi Maragheh M, Khayatzadeh Mahani M, Aliabadi M (2008) Determination of ^{90}Sr concentration in soil and sediment samples from Southern Shores of Iran using a Sr Resin and LSC method. In: Eikenberg J, Jäggi M, Beer H, Baehrle H (ed) LSC 2008, Advances in Liquid Scintillation Spectrometry, Davos, May 25-30, 2008. Radiocarbon, Tuscon, 299-303

[9] Gastberger M, Steinhäusler F, Gerzabek MH, Lettner H, Hubmer A (2000) Soil-to-plant transfer of fallout caesium and strontium in Austrian lowland and Alpine pastures. J Environ Radioact 49:217-233

[10] Silva CM, Amaral RS, Tabosa JN, Santos Junior JA, Menezes RSC, Farias EEG, Bezerra JD, Silvestre RG, Oliveira GF (2009) Pb-210 in rock and soils of the semi-arid agreste region of Pernambuco, Brazil. Bull Environ Contam Toxicol 82:647-649

[11] Everithing2: Last update Dec 2006. Available: http://everything2.com/title/The+Poisoning+of+Alexander+Litvinenko. Accessed May 2011

[12] Navrátil O, Hála J, Kopunec R, Lešetický L, Macášek F, Mikulaj V (1985) Nuclear Chemistry. Academia, Praha

[13] Warner SF, Harrison RM (1993) SCOPE 50 - Radioecology after Chernobyl: Biogeochemical Pathways of Artificial Radionuclides. John Wiley & Sons, Chichester

[14] Chopin G, Liljenzin JO, Rydberg J (2002) Radiochemistry and nuclear chemistry, 3rd edn. Butterworth-Heineman, Woburn

[15] United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) (2000) Sources and effects of ionizing radiation, vol I. United Nations, New York

[16] United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) (1993) Sources and effects of ionizing radiation, vol I. United Nations, New York

[17] Remy H (1971) Anorganicka chemie, I. dil. SNTL, Praha

[18] Lide DR (2004) Handbook of chemistry and physics, 84th edn. CRC Press, Boca Raton

[19] Tölgyessy J, Harangozó M (2000) Radioecology, 1st edn. Matej Bel University – Faculty of Natural Sciences, Banska Bystrica

[20] Zhang A, Wei YZ, Kumagai M, Koyama T (2004) Kinetics of the adsorption of strontium (II) by a novel silica-based 4,4´,(5´)-di(tert-butylcyclohexano)-18-crown-6 extraction resin in nitric acid medium. J Radioanal Nucl Chem 262(3):739-744

[21] Goutelard F, Nazard R, Bocquet C, Coquenlorge N, Letessier P, Calmet D (2000) Improvement in ^{90}Sr measurements at very low levels in environmental samples. Appl Radiat Isot 53:145-151

[22] Fresquez PR, Biggs JR, Bennett KD, Kraig DH, Mullen MA, Ferenbaugh JK (1999) Radionuclides in deer and elk from Los Alamos National Laboratory and the doses to humans from the ingestion of muscle and bone. J Environ Sci Health B34(5):901-915

[23] Mangano JJ, Gould JM, Sternglass EJ, Sherman JD, McDonnell W (2003) An unexpected rise in strontium-90 in US deciduous teeth in the 1990s. Sci Total Environ 317:37-51

[24] Bjornstad HE, Lien HN, Yu Y-F, Salbu B (1992) Determination of ^{90}Sr in environmental and biological materials with combined HDEHP solvent extraction – low liquid scintillation counting technique. J Radioanal Nucl Chem 156(1):165-173

[25] Landstetter C, Cernohlawek N, Katzlberger C (2008) Determination of ^{90}Sr in milk in Austria. In: Eikenberg J, Jäggi M, Beer H, Baehrle H (ed) LSC 2008, Advances in Liquid Scintillation Spectrometry, Davos, May 25-30, 2008. Radiocarbon, Tuscon, 313-319

[26] Tiller BL, Poston TM (2000) Mule deer antlers as biomonitors of strontium-90 on the Hanford Site. J Environ Radioact 47:29-44

[27] Nygren U (1999) Determination of ^{90}Sr in soil and sediment using lithium-borate fusion and extraction chromatography. J Radioanal Nucl Chem 241(3):549-551

[28] Daniel C, Pin C (2001) Single-stage method for the simultaneous isolation of lead and strontium from silicate samples for isotopic measurements. Analyt Chim Acta 426:95-103

[29] Alvarez A, Navarro N, Salvador S (1995) New method for for ^{90}Sr determination in liquid samples. J Radioanal Nucl Chem 191(2):315-322

[30] Tatzber F, Irlweck K (1984) Accumulation of fallout nuclides and natural radioactivity in Austrian snails. Health Phys 46(2):448-452

[31] Irlweck K, Khademi B (1996) Radionuclide ratios of ^{90}Sr/^{137}Cs and $^{239(240)}$Pu/^{137}Cs in contaminated surface air after the Chernobyl accident in Austria. J Radioanal Nucl Chem 203(1):79-85

[32] Juznic K, Fedina S (1986) Radiochemical determination of ^{90}Sr and ^{89}Sr in soil. Fresenius Z Anal Chem 323:261-263

[33] Schönhofer F, Tataruch F, Friedrich M (1994) Strontium-90 in antlers of red deer: an indicator of environmental contamination by strontium-90. Sci Total Environ 157: 323-332

[34] Kagawa A, Aoki T, Okada N, Katayama Y (2002) Tree-ring Strontium-90 and Cesium-137 as potential indicators of radioactive pollution. J Environ Qual 31:2001-2007

[35] Florou H, Savidou A, Chaloulou C (1996) Strontium-90 activity in monthly milk samples from Greece. J Dairy Sci 79:1679-1682

[36] Bossew P, Ichikawa M, Mraz G, Wallner G, Wenisch A (2000) Radiological investigations in the surroudings of Bilibino, Chukotka, Russia. J Environ Radioact 51:299-319

[37] Tatzber F, Irlweck K, Schaller F (1982) Falloutradionuklide und natürliche Radioaktivität in Rehgewebeproben aus verschiedenen Gebieten Österreichs. Wien Tierärztl Mschr 69(3):86-93

[38] HASL-300, Sr-01-RC, Sr-02-RC, 28th edition (1997) In: Chieco, N.A. (ed.), The Procedures manual of the Environmental Measurements Laboratory, vol. II. U.S. Department of Energy, New York

[39] Brun S, Kergadallan Y, Boursier B, Fremy JM, Janin F (2003) Methodology for determination of radiostrontium in milk: a review. Lait 83:1-15

[40] Popov L, Mihailova G, Hristova I, Dimitrova P, Tzibranski R, Avramov V, Naidenov I, Stoenelova B (2009) Separation of strontium from calcium by the use of sodium hydroxide and its application for the determination of long-term background activity concentrations of ^{90}Sr in 100 km area around Kozloduy Nuclear Power Plant (Bulgaria). J Radioanal Nucl Chem 279(1):49-64

[41] Popov L, Mihailova G, Naidenov I (2010) Determination of activity ratios of $^{238,239+240,241}$Pu, ^{241}Am, ^{134,137}Cs, and ^{90}Sr in Bulgarian soils. J Radioanal Nucl Chem 285:223-237

[42] Chen Q, Hou X, Yu Y, Dahlgaard H, Nielsen SP (2002) Separation of Sr from Ca, Ba and Ra by means of $Ca(OH)_2$ and $Ba(Ra)Cl_2$ or $Ba(Ra)SO_4$ for the determination of radiostrontium. Analyt Chim Acta 466:109-116

[43] Weiss HV, Shipman WH (1957) Separation of strontium from calcium with potassium rhodizonate. Anal Chem 29(12):1764-1766

[44] Bunzl K, Kracke W (1991) A simple radiochemical determination of ^{90}Sr in environmental samples. J Radioanal Nucl Chem 148(1):115-119

[45] Klouda P (2003) Moderní analytické metódy. Nakladatelství Pavel Klouda, Ostrava

[46] Martin JE (1987) Measurement of ^{90}Sr in reactor wastes by Cerenkov counting of ^{90}Y. Appl Radiat Isot 38(11):953-957

[47] Baratta EJ, Ferri ES (1967) Determination of strontium-90 in human bones by tributyl phosphate. Anal Chem 39(7):846-847

[48] Mietelsky JW, LaRosa J, Ghods A (1993) ^{90}Sr and $^{239+240}$Pu ^{238}Pu ^{241}Am in some samples of mushrooms and forest soil from Poland. J Radioanal Nucl Chem 170 (1):243-258

[49] Lapid J, Miinster M, Farhi S, Eini M, Lalouche L (1984) A rapid method for the determination of radiostrontium in river water. J Radioanal Nucl Chem 86 (5):321-326

[50] Mikulaj V, Svec V (1993) Radiochemical analysis of ^{90}Sr in milk, soil and plants by solvent extraction. J Radioanal Nucl Chem 175(4):317-324

[51] Bem H, Bakir YY, Shuker SM (1991) A rapid method for the determination of strontium-90 in powdered milk. J Radioanal Nucl Chem 147(2):263-268

[52] Shabana EI, Al-Hussan KA, Al-Jaseem QK (1996) Adaptation of a radioanalytical method for strontium-90 to different kinds of environmental samples and its application for the investigation of some samples in the Riyadh region. J Raioanal Nucl Chem 212(3):229-240

[53] Chang Z, Diao L, Jiang S, Li A, Zhao M, Zhao Y (2004) Determination of ^{90}Sr and ^{137}Cs concentrations in the IAEA reference material Soil-6. J Radioanal Nucl Chem 260(1):61-68

[54] Solecki J, Chibowski S (2002) Studies on horizontal and vertical migration of ^{90}Sr in soil systems. Polish J Environ St 11(2):157-163

[55] Borcherding J, Nies H (1986) An improved method for the determination of ^{90}Sr in large samples of seawater. J Radioanal Nucl Chem 98(1):127-131

[56] Pedersen CJ (1967) Cyclic polyethets and their complexes with metal salts. J Am Chem Soc 89:7017-7036

[57] Gokel GW, Leevy WM, Weber ME (2004) Crown ethers: sensors for ions and molecular scaffolds for materials and biological models. Chem Rev 104:2723-2750

[58] Kimura T, Iwashima K, Ishimori T, Hamaguchi H (1977) Separation of strontium ion from a large amount of calcium ion by the use of macrocyclic ether. Chem Lett 563-564

[59] Vaney B, Friedli C, Geering JJ, Lerch P (1989) Rapid trace determination of radiostrontium in milk and drinking water. J Radioanal Nucl Chem 134(1):87-95

[60] Visser AE, Swatloski RP, Reichert WM, Griffin ST, Rogers RD (2000) Traditional extractants in nontraditional solvents: groups 1 and 2 extraction by crown ethers in room-temperature ionic liquids. Ind Eng Chem Res 39:3596-3604

[61] Horwitz EP, Dietz ML, Fisher DE (1990) Extraction of strontium from nitric acid solutions using dicyclohexano-18-crown-6 and its derivates. Solvent Extr Ion Exch 8:557-572

[62] Marhol M (1976) Meniče iontú v chemii a radiochemii. Academia, Praha

[63] Grahek Z, Eskinja I, Kosutic K, Lulic S, Kvastek K (1999) Isolation of radioactive strontium from natural samples: separation of strontium from alkaline earth elements by means of mixed solvent anion exchange. Anal Chim Acta 379:107-119

[64] Al-Merey R, Al-Shayah O (2003) Ion exchange separation of lead from strontium in certified reference samples and spectrophotometric determination of lead as extractable ion-pair of eosin^{2-} and the lead-cryptand (2.2.2)$^{2+}$ complex. J Trace Microprobe Tech 21(1):13-24

[65] Grahek Z, Eskinja I, Kosutic K, Stefanovic SC (2000) Isolation of yttrium and strontium from soil samples and rapid determination of ^{90}Sr. Croat Chem Acta 73(3):795-807

[66] Horwitz EP: Extraction chromatography of actinides and selected fission products: Principles and achievement of selectivity. Last update: 2010. Available: http://www.eichrom.com/products/extraction.cfm. Accessed March 2011

[67] Zwir-Ferenc A, Biziuk M (2006) Solid phase extraction technique – trends, opportunities and applications. Polish J Environ Stud 15(5):677-690

[68] Vajda N, Ghods-Esphahani A, Cooper E, Danesi PR (1992) Determination of radiostrontium in soil samples using a crown ether. J Radioanal Nucl Chem 162(2):307-323

[69] Dietz ML, Horwitz EP, Nelson DM, Wahlgren M (1991) An improved method for determining ^{89}Sr and ^{90}Sr in urine. Health Phys 61(6):871-877

[70] Horwitz EP, Dietz ML, Fisher DE (1991) Separation and preconcentration of strontium from biological, environmental, and nucleare waste samples by extraction chromatography using a crown ethers. Anal Chem 63:522-525

[71] Horwitz EP, Chiarizia R, Dietz ML (1992) A novel strontium-selective extraction chromatographic resin. Solvent Extr Ion Exch 10(2):313-336

[72] Jakopic R, Benedik L (2005) Trace studies on Sr Resin and determination of ^{90}Sr in environmental samples. Acta Chim Slov 52:297-302

[73] Landstetter C, Ringer W, Achatz A, Katzlberger C (2010) Determination of ^{90}Sr in soil, grass and cereals. J Radioanal Nucl Chem 286:435-439

[74] Mietelski JW, Gaca P, Zagrodzki P, Jasinska M, Zalewski M, Tomczak M, Vajda N, Dutkiewicz EM (2001) ^{90}Sr and stable strontium in bones of wild, herbivorous animals from Poland. J Radioanal Nucl Chem 247(2):363-370

[75] Grahek Z, Kosutic K, Rozmaric-Macefat M (2006) Strontium isolation from natural samples with Sr resin and subsequent determination of ^{90}Sr. J Radioanal Nucl Chem 268(2):179-190

[76] Saxén R (2002) Determination of ^{90}Sr by extraction chromatography in the presence of ^{210}Pb in environmental samples. In: Möbius S, Noakes J,

Schönhofer F (ed) LSC 2001, Advances in Liquid Scintillation Spectrometry. Radiocarbon, Tuscon 389-395

[77] Mietelski JW, Kitowski I, Gaca P, Grabowska S, Tomankiewicz E, Szwalko P (2006) Gamma-emitters ^{90}Sr, $^{238,239+240}$Pu and ^{241}Am in bones and liver of eagles from Poland. J Radioanal Nucl Chem 270(1):131-135

[78] Michel H, Levent D, Barci V, Barci-Funel G, Hurel C (2008) Soil and sediment sample analysis for the sequential determination of natural and anthropogenic radionuclides. Talanta 74:1527-1533

[79] Wang JJ, Chen IJ, Chiu JH (2004) Sequential isotopic determination of plutonium, thorium, americium, strontium and uranium in environmental and bioassay samples. Appl Radiat Isot 61:299-305

[80] Moreno J, Vajda N, Danesi PR, Larosa JJ, Zeiller E, Sinojmeri M (1997) Combined procedure for the determination of ^{90}Sr, ^{241}Am and Pu radionuclides in soil samples. J Radioanal Nucl Chem 226(1-2):279-284

[81] Brun S, Bessac S, Uridat D, Boursier B (2002) Rapid method for the determination of radiostrontium in milk. J Radioanal Nucl Chem 253(2):191-197

[82] Schmitz M, Schmitz K, Aumann DC (2004) A simple radiochemical method for determining bone-seeking radionuclides in bone and teeth: ^{90}Sr in teeth of children from Ukraine and Germany. J Radioanal Nucl Chem 260(3):451-457

[83] Tavcar P, Jakopic R, Benedik L (2005) Sequential determination of ^{241}Am, ^{237}Np, Pu radioisotopes and ^{90}Sr in soil and sediment samples. Acta Chim Slov 52:60-66

[84] Smith LL, Orlandini KA, Alvarado JS, Hoffman KM, Seely DC, Shannon RT (1996) Application of Empore™ strontium Rad disks to the analysis of radiostrontium in environmental water samples. Radiochim Acta 73:165-170

[85] Bradshaw JS, Izatt RM (1997) Crown ethers: the search for selective ion ligating agents. Acc Chem Res 30:338-345

[86] Izzat SR, Bruening RL, Krakowiak KE, Izatt RM (2003) The selective separation of anions and cations in nuclear waste using commercially available molecular recognition technology (MRT) products. In: WM 03 Conference, February 23-27, 2003. Tuscon

[87] Smith LL, Orlandini K (1999) Radiochemical analysis using Empore Rad Disks. Global ´99: “Nuclear Technology – Bridging the Millennia” , Proceedings of the International Conference on Future Nuclear Systems, Jackson Hole, WY, United States, 1930-1934

[88] Fiskum SK, Riley RG, Thompson CJ (2000) Preconcentratration and analysis of strontium-90 and technetium-99 from Hanford groundwater using solid phase extraction. J Radioanal Nucl Chem 245(2):261-272

[89]. Svehla G (1979) Vogel´s textbook of macro and semimicro qualitative inorganic analysis, 5th edition, Longman, New York

[90] Galanda D, Rajec P, Mátel L, Rosskopfová O, Dulanská S (2009) Separation techniques for quantification of radionuclides in environmental samples. The Sci World J 9:1206-1214

[91] Beals DM, Britt WG, Bibler JP, Brooks DA (1998) Radionuclide analysis using solid phase extraction disks. J Radioanal Nucl Chem 236(1-2):187-191

[92] Kameo Y, Katayama A, Fujiwara A, Haraga T, Nakashima M (2007) Rapid determination of ^{89}Sr and ^{90}Sr in radioactive waste using Sr extraction disk and beta-ray spectrometer. J Radioanal Nucl Chem 274(1):71-78

[93] Chu TC, Wang JJ, Lin YM (1998) Radiostrontium analytical method using crown-ether compound and Cerenkov counting and its applications in environmental monitoring. Appl Radiat Isot 49(12):1671-1675

[94] Rajec P, Mátel L, Rosskopfová O, Dulanská S, Galanda D (2009) Determination of radionuclides in environmental samples. New Techniques for Detection of Nuclear and Radioactive Agents. Spinger, 273-285

[95] Galamboš M, Kufčáková J, Rajec P (2009) Adsorption of cesium on domestic bentonites. J Radioanal Nucl Chem 281:485-492

[96] Taylor HW, Svoboda J, Henry GHR, Wein RW (1988) Post-Chernobyl ^{134}Cs and ^{137}Cs levels at some localities in northern Canada. Arctic 41(4):293-296

[97] ElnSamad O, Zahraman K, Baydoun R, Nasreddine M (2007) Analysis of radiocaesium in the Lebanese soil one decade after the Chernobyl accident. J Environ Radioact 92:72-79

[98] Degerlier M, Karahan G, Ozger G (2008) Radioactivity concentrations and dose assessment for soil samples around Adana, Turkey. J Environ Radioact 99:1018-1025

[99] Tzortzis M, Tsertos H, Christofides S, Christodoulides G (2003) Gamma radiation measurements and dose rates in commercially-used natural tiling rocks (granites). J Environ Radioact 70:223-235

[100] Papastefanou C, Stoulos S, Manolopoulou M (2004) The radioactivity of building materials. J Radioanal Nucl Chem 266(3):367-372

[101] Abbady AGE, Uosif MAM, El-Taher A (2005) Natural radioactivity and dose assessment for phosphate rocks from Wadi El-Mashash and El-Mahamid Mines, Egypt. J Environ Radioact 84:65-78

[102] El Afifi EM, Borai EH (2006) Performance characteristics of sequential separation and quantification of lead-210 and polonium-210 by ion exchange chromatography and nuclear spectrometric measurements. J Environ Qual 35:568-574

[103] Miura T, Hayano K, Nakayama K (1999) Determination of ^{210}Pb and ^{210}Po in environmental samples by alpha ray spectrometry using an extraction chromatographic resin. Anal Sci 15:23-28

[104] Nieri Neto A, Mazzilli B (1998) Evaluation of ^{210}Po and ^{210}Pb in some mineral spring waters in Brazil. J Environ Radioact 41(1):11-18

[105] Peres AC, Hiromoto G (2002) Evaluation of ^{210}Pb and ^{210}Po in cigarette tobacco produced in Brazil. J Environ Radiat 62:115-119

[106] Kelecom A, Gouvea RCS, Santos PL (2002) Levels of ^{210}Po and ^{210}Pb in cigars. J Radioanal Nucl Chem 253(1):129-133

[107] Katzlberger C, Wallner G, Irlweck K (2001) Determination of ^{210}Pb, ^{210}Bi and ^{210}Po in natural drinking water. J Radioanal Nucl Chem 249(1):191-196

[108] El Afifi EM (2005) Asessment of ^{210}Pb in different samples using developed radiochemical methods. Arab J Nucl Sci Appl 38(1):73-81

[109] Tosheva Z, Kies A, Klosen M, Veltchev K (2004) Determination of ultra-low concentrations of Pb-210 in Antarctic glacier with cation exchange resins filter-results, problems and perspectives. Appl Radiat Isot 61:267-271

[110] Klevezal GA, Bakhur AE, Kalyakin VN, Krushinskaya NL (2001) Dynamics of radionuclide concentrations in calcified tissues of reindeer in the western Russian Arctic. Chemosphere 42:61-67

[111] Miura T, Hayano K, Nakayama K (1999) Determination of ^{210}Pb and ^{210}Po in environmental samples by alpha ray spectrometry using an extraction chromatographic resin. Anal Sci 15:23-28

[112] Clayton RF, Bradley EJ (1995) A cost effective method for the determination of 210Po and 210Pb in environmental materials. Sci Total Environ 173/174:23

[113] Irlweck K, Wallner G (1993) Determination of ^{226}Ra in lake sediments by liquid scintillation counting of cocktail-extracted ^{222}Rn. In: Noakes JE, Schönhofer F, Polach HA (ed) LSC 1992, Radiocarbon, Tuscon 391

[114] Lieser KH (2001) Nuclear and radiochemistry. Fundamentals and applications, 2nd edn. Wiley-Vch, Weinheim

[115] Quantulus 1220 Liquid Scintillation Counter (1989) Instrumental manual, LKB Wallac

[116] Canberra, Germanium detectors, User's manual (2003) Canberra Industries, Meriden

[117] Agilent 7500 Series ICP-MS (2008) Hardware Manual, Agillent Technologies, USA

2 Results

The main results of my doctoral thesis are based on following publications:

Isolation and measurement of strontium-90 and lad-210 in environmental samples using a strontium-specific resin and liquid scintillation counting

Wallova G, Wallner G (2009) In: Eikenberg J, Jäggi M, Beer H, Baehrle H (ed) LSC 2008, Advances in Liquin Scintillation Spectrometry, Davos, Switzerland, May 25-30, 2008, Radiocarbon, Tuscon, 367-373

Wallner G. conceived the initial idea; Wallova G. expanded the initial idea. Wallova G. conducted experimental part (preparation of samples, radioanalytical separations, measurements using LCS). Wallova G. assisted with ICP-MS measurements. Wallova G. wrote the manuscript. Wallner G. assisted in reviewing the article and helpful discussions.
Contribution of Wallova G. to the article: 80%.

Determination of ^{90}Sr and ^{210}Pb in deer bone samples by liquid scintillation counting after ion-exchange procedures

Wallova G, Kandler N, Wallner G (2010) J Radioanal Nucl Chem 286:429-433

Wallner G. and Wallova G. conceived the initial idea. Wallova G. conducted experimental part (preparation of samples, radioanalytical separations, measurements using LSC). Wallova G. assisted with ICP-MS measurements. Kandler N. conducted ICP-MS measurements. Wallova G. wrote the manuscript. Wallner G. assisted in reviewing the article and helpful discussions.
Contribution of Wallova G. to the article: 75%.

Monitoring of radionuclides in soil and bone samples from Austria

Wallova G, Kandler N, Wallner G (May, 2011) revised manuscript submitted in J Environment Radioact

Wallner G. and Wallova G. conceived the initial idea. Wallova G. conducted experimental part (preparation of samples, radioanalytical separations, measurements using LSC). Wallova G. assisted with ICP-MS measurements. Kandler N. conducted ICP-MS measurements. Wallova G. wrote the experimental part of manuscript. Wallner G. wrote the article.
Contribution of Wallova G to the article: 70%.

Fast determination of Po-210 in urine by LSC as a means to estimate deliberate poisioning

Wallner G, Schönhofer F, Wallova G, Steger F (Okt. 2010) revised manuscript submitted in LSC 2010, Advances in Liquin Scintillation Spectrometry, 6-10 September 2010, Paris, France, Radiocarbon, Tuscon

Wallner G. and Schönhofer F. conceived the initial idea. Wallova G. and Wallner G. expanded the initial idea and conducted experimental part (preparation of samples, radioanalytical separations, measurements using LSC). Wallner G. wrote the manuscript. Schönhofer F., Steger F. assisted with helpful discussions and reviewing of article.
Contribution of Wallova G. to the article: 40%.

Within the scope of this thesis I contributed to the following article. This article is not included in thesis because it was used for attaining of RNDr. degree on Comenius University in Bratislava.

Determination of naturally occurring radionuclides in selected rocks from Hetaunda area, central Nepal

Wallova G, Acharya KK, Wallner G (2010) J Radioanal Nucl Chem 283: 713-718

Wallova G. and Wallner G. conceived the initial idea. Acharya K. K. did the sampling, developed the geographical and geological map. Wallova G. conducted experimental part (performed all gamma measurements and data evaluations). Wallova G. wrote the manuscript. Wallner G. assisted in reviewing of article and helpful discussions.
Contribution of Wallova G. to the article: 75%.

2.1 Isolation and measurement of strontium-90 and lad-210 in environmental samples using a strontium-specific resin and liquid scintillation counting

Wallova G, Wallner G (2009) In: Eikenberg J, Jäggi M, Beer H, Baehrle H (ed) LSC 2008, Advances in Liquin Scintillation Spectrometry, Davos, Switzerland, May 25-30, 2008, Radiocarbon, Tuscon, 367-373

ISOLATION AND MEASUREMENT OF STRONTIUM-90 AND LEAD-210 IN ENVIRONMENTAL SAMPLES USING A STRONTIUM-SPECIFIC RESIN AND LIQUID SCINTILLATION COUNTING

Gabriela Wallova[1] • Gabriele Wallner

Institut für Anorganische Chemie, Universität Wien, Währinger Str. 42, A-1090 Vienna, Austria.

ABSTRACT. A separation procedure for ^{90}Sr and ^{210}Pb in animal bones and soil samples was developed. The method comprises sequential separation of Pb from other cations on Dowex with subsequent Sr isolation on SrSpec® resin. ^{90}Sr and ^{210}Pb activities were measured by liquid scintillation spectrometry. Our results for the reference sample IAEA soil-135 were in excellent agreement with the certified values. A soil profile that had already been investigated recently was remeasured and good agreement was found between the 2 sets of data.

INTRODUCTION

^{90}Sr is one of the most hazardous fission products due to its chemical similarity with calcium and its ensuing high transfer rate to the skeleton. ^{90}Sr is a beta emitter with a maximum β energy of 0.5 MeV and half-life of 28.5 yr; its short-lived daughter ^{90}Y (half-life 64.1 hr) emits hard beta particles with a maximum energy of 2.3 MeV. From the radiation protection point of view, it is very important to control ^{90}Sr in the environment and in food (Hardy et al. 1968). Although there exist data from deer, roe deer, reindeer, and elk (Tatzber et al. 1982; Strandberg and Strandgaard 1995; Tiller and Poston 1999; Klevezal et al. 2001; Mietelski et al. 2001; Landstetter and Wallner 2006), generally ^{90}Sr data for environmental samples are relatively scarce. As the investigated animals are at the end of a complicated radioecological foodchain, from these samples we cannot gain information about deposition densities after fallout or about migration rates in different soil types. Thus, we intend to also collect soil samples in all regions from where deer bone samples were delivered to us, in order to fill that gap of knowledge. Our method for strontium extraction, originally developed for bone samples and then applied to soil samples with some modification, is tested here for the much more complex soil samples.

^{90}Sr separation from samples like soil, food, milk, deer bones, etc., by using SrSpec® resin (Eichrom Industries, Inc.) in prepacked columns (2 mL of resin) is reported in the literature (see e.g. Horwitz et al. 1991; Alvarez et al. 1995; Shabana et al. 1996; Brun et al. 2002; Vrcek et al. 2004; Landstetter and Wallner 2006). After separation, ^{90}Sr is usually measured by liquid scintillation counting (LSC) or using gas-flow proportional counters. However, not only strontium, but also lead and therefore ^{210}Pb, which is present in soil as well as bone samples, is retained by SrSpec from nitric acid solutions (Dietz et al. 1991; Horwitz et al. 1992). In order to get pure ^{90}Sr LSC spectra, the condition for the ^{90}Sr elution can be chosen so that lead remains on the column (Landstetter and Wallner 2006). In this work, lead is separated by anion exchange before strontium purification, as this will enable us to measure also the ^{210}Pb activity in our samples, giving the possibility to compare the uptake of an anthropogenic and a natural radionuclide. ^{210}Pb (half-life 22.3 yr), emitting betas ($E_{\beta,max}$ = 63 keV (20%) and 16.5 keV (80%)) and electrons from the highly converted γ decay (46.5 keV), can also be measured by LSC with 100% detection efficiency (Wallner 2002).

Strontium and lead must be separated from many interfering elements like calcium, magnesium, barium, radium, and iron. First, we investigated the separation of Pb from Sr by using different

[1]Corresponding author. Email: gabriela.wallova@univie.ac.at.

LSC 2008, Advances in Liquid Scintillation Spectrometry
edited by J Eikenberg, M Jäggi, H Beer, H Baehrle, p 367–373

anion-exchange columns, then Sr was purified on a SrSpec column. For soil samples, an additional precipitation step for Sr preconcentration is recommended.

EXPERIMENTAL

Reagents and Equipment

All reagents were of analytical grade: 65% HNO_3, 37% HCl, 45% HF, H_3BO_3, 25% NH_3, all purchased from Merck; 1-octanol, purchased from Fluka. Analytical-grade ion-exchange resins included Dowex 1 × 4 (Cl^- form, 100–200 mesh), Dowex 1 × 2 (Cl^- form, 100–200 mesh), Dowex 1 × 8 (Cl^- form, 20–50 mesh), Dowex 1 × 8 (Cl^- form, 100–200 mesh), all from Fluka; and SrSpec Resin (100–150 µm) from Eichrom, USA.

Standard solutions of Sr^{2+}, Pb^{2+}, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Fe^{3+}, and Cr^{3+} were prepared from appropriate salts by dissolution in 1M HCl and 0.5M HBr.

The equipment used included a mechanical shaker (Heidolph PROMAX 1020, Germany), and ICP-MS (Agilent 7500ce, Waldbronn, Germany, equipped with a CETAC ASX-520 autosampler); and an LS counter, Quantulus 1220, WallacOy, Finland (now PerkinElmer).

Preparation of a "Bone Standard Solution"

To investigate different separation methods, a standard solution containing various cations in 0.5M HBr and 1.5M HCl, respectively, were prepared to simulate the mineral composition found in animal bones (Taylor et al. 1960; Beighle et al. 1994; D'Haese et al. 1996; Staub et al. 2003): Ba^{2+}: 0.02 mg/mL solution; Ca^{2+}: 1 mg/mL; Fe^{3+}: 0.132 mg/mL; Cr^{3+}: 0.002 mg/mL; K^+: 0.037 mg/mL; Mg^{2+}: 1 mg/mL; Na^+: 1 mg/mL; Pb^{2+}: 0.05 mg/mL; Sr^{2+}: 0.05 mg/mL. One mL of this solution was then loaded on the respective Dowex columns (8 mm internal diameter, 15 cm high).

Separation of Pb Using Dowex Anion Exchanger and Hydrobromic/Hydrochloric Acid

These separation methods are modified versions of the methods previously published by Vajda et al. (1992), Al-Merey and Al-Shayah (2003), and Michel et al. (2008). The exchangeable anion Cl^- was replaced by Br^- by shaking a Dowex 1 × 4 (Cl^- form, 100–200 mesh) overnight on a mechanical shaker with a solution of 6M HBr. The resin was then mixed with 30 mL of 0.5M HBr and shaken again for 1 hr.

In the column, a thin layer of glass wool was laid on top of the resin, which was finally washed with 50 mL of 0.5M HBr. One mL of the above-described "bone standard solution" (salts in 0.5M HBr) was passed through the column with a flow rate of 1 mL/min. Then, the column was washed with 50 mL of 0.5M HBr. This rinsing solution containing Sr^{2+} and all cations listed above (with the exception of Pb^{2+}) was collected for further analysis. Subsequently, the column was washed with 50 mL of 6M HBr at the same flow rate to elute Pb^{2+}. Both solutions were evaporated to dryness, dissolved in 2% HNO_3, and measured by inductively coupled plasma mass spectrometry (ICP-MS). The column was then prepared for the next cycle by rinsing with 50 mL of 6M HBr, 50 mL of distilled water, and finally with 50 mL of 0.5M HBr.

For Pb determination from hydrochloric acid, Dowex 1 × 4 (Cl^- form, 100–200 mesh) was soaked in 1.5M HCl for approximately 24 hr. After loading onto the column, it was rinsed with 1.5M HCl until free from impurities (~50 mL). One mL of the "bone standard solution" (salts in 1.5M HCl) was passed through the column with a flow rate of 1 mL/min. The column was washed with 50 mL of 1.5M HCl and Pb^{2+} was eluted with 50 mL of 0.05M HCl at the same flow rate. All fractions were measured by ICP-MS.

The separations using Dowex 1 × 2 (100–200 mesh), Dowex 1 × 8 (20–50 mesh), and Dowex 1 × 8 (100–200 mesh) (all in 1.5M HCl) were done in the same way as described for Dowex 1 × 4 in 1.5M HCl. Table 1 shows the results of the Pb separation by using different anion exchangers. Sr and Pb concentrations are determined by ICP-MS. Sr, which is not held back on the Dowex columns, is found with high yield (>87%) in the effluent. When using Dowex 1 × 4 (100–200 mesh) in HBr or Dowex 1 × 8 (20–50 mesh or 100–200 mesh) in HCl, the Sr yield is nearly 100%. The yield in the Pb fraction, however, is satisfactory only in the case of Dowex 1 × 8 (100–200 mesh). Therefore, Dowex 1 × 8 (100–200 mesh) in 1.5M HCl was used for quantitative ^{210}Pb and ^{90}Sr determination in our bone and soil samples.

Table 1 Separation of Pb from Sr using different anion exchange columns.

Experiment nr	Method	Medium	Sr fraction ch. yield (%)	Pb fraction ch. yield (%)
1	Dowex 1 × 4, 100–200 mesh	HBr	99.6 Sr 0.5 Pb	1.4 Pb 0.04 Sr
2	Dowex 1 × 4, 100–200 mesh	HCl	92.2 Sr 1.4 Pb	68.2 Pb 0.3 Sr
3	Dowex 1 × 2, 100–200 mesh	HCl	87.5 Sr 3.7 Pb	14.7 Pb 0.2 Sr
4	Dowex 1 × 8, 20–50 mesh	HCl	99.6 Sr 1.2 Pb	82.8 Pb 0.2 Sr
5	Dowex 1 × 8, 100–200 mesh	HCl	99.7 Sr 0 Pb	98 Pb 0 Sr

Along with the "bone standard solution" a chemical blank value of 1.8 cpm (counts per minute) in the ^{210}Pb region was also determined. With a maximum counting time of 1000 min, the lower limit of detection (LLD), given by the formula of Seymour et al. (1992), was 4 Bq/kg ^{210}Pb (a sample mass of 1 g and a chemical yield of 80% was assumed).

Purification of Sr by SrSpec Resin

After separation of Pb, the Sr fraction has to be purified from other interfering ions, such as Ca^{2+}, Ra^{2+}, and Y^{3+}. The separation follows the method published by Landstetter and Wallner (2006).

The 1.5M HCl effluent from the Dowex column containing Sr is evaporated to dryness and the residue is converted to nitrates by adding concentrated HNO_3. After repeated evaporation, the residue was taken up in 20 mL of 8M HNO_3 saturated with 1-octanol. This solution was loaded onto the SrSpec column. The column was consequently rinsed with 50 mL 8M HNO_3 and 100 mL 3M HNO_3 (also saturated with 1-octanol) to remove the alkaline earth metals. Strontium was stripped with 30 mL of distilled water and measured by ICP-MS. Real samples containing radiostrontium were measured by LSC after volume reduction to 8 mL of water and mixing with 12 mL HiSafe™ III cocktail.

By measuring a standard solution directly mixed with the scintillation cocktail, the ^{90}Sr counting efficiency was found to be 100% when using a counting window that comprises the whole ^{90}Sr peak (Landstetter and Wallner 2006). Again, the "bone standard solution" was also used to determine a chemical blank value: 1.8 cpm in the ^{90}Sr region was measured. With a maximum counting time of 1000 min, the LLD (following Seymour et al. 1992) was 7 Bq/kg ^{90}Sr (again a sample mass of 1 g and a chemical yield of 80% was assumed).

Sample Preparation

Bone Samples

After ashing for 17–22 hr at 450 °C, the samples were ground and weighed. One g of bone ash was dissolved in 5 mL of 8M HNO_3, while 10 mg of Sr^{2+} carrier (as strontium nitrate) and 20 mg of Pb^{2+} carrier (as lead nitrate) were added for chemical yield determination. The solution was boiled under reflux for 3 hr, filtrated, and evaporated until dry; the residues were dissolved in 70 mL of 1M HNO_3. For chemical yield determination by ICP-MS, an aliquot of 2.5 mL is taken for the analyses. Afterwards, the sample was again evaporated to dryness and the residues were converted to the chlorides by evaporating 3 times with concentrated HCl; at the end, the sample was dissolved in 10 mL of 1.5M HCl and loaded on the Dowex 1 × 8 (100–200 mesh) column for Pb separation. (Sr is not held back on the column; it is in the 1.5M HCl effluent, see below.)

The Pb was eluted with 70 mL of 0.05M HCl and 10 mL of water. This solution was evaporated to dryness (1.5 mL of the solution was taken for ICP-MS yield measurement), redissolved with 1 mL of 65% HNO_3, and again evaporated. This step was repeated 3 times to destroy any organic contaminations from the resin. The residue was dissolved in 2 mL of 2M HNO_3; this solution was mixed with 18 mL of HiSafe III scintillation cocktail and ^{210}Pb was measured by LSC.

If an ICP-MS measurement was not possible, the chemical yield was determined by gravimetry (El Afifi and Borai 2006). The residue left after destroying any organic matter was dissolved in 20 mL of 1M HNO_3, stirred, warmed, and mixed with 0.4 g of oxalic acid. The pH was adjusted to approximately 3 using 25% NH_3. After 30 min, the Pb oxalate precipitate was collected on a filter under vacuum. After washing with distilled water and 80% ethanol, the precipitate was dried in an oven at 50 °C for 30 min. The precipitate was weighed for the gravimetric calculations of the recovery. After that, the Pb oxalate precipitate was dissolved in 2 mL of 2M HNO_3 and measured by LSC.

The 1.5M HCl effluent from the Dowex column containing Sr is processed as described above. Also, here we used an oxalate precipitation for gravimetric chemical yield determination as an alternative to ICP-MS measurements. Sr oxalate is precipitated in the same way as described above for Pb oxalate, but precipitation takes place at pH = 9–10. The procedures for gravimetry, redissolution, and LSC measurement were the same.

Soil Samples

The ground and sieved (≤100 mesh) samples were ashed in a silica dish for about 20 hr at 550 °C. To 10 g of this sample, 10 mL of 1M HNO_3, 10 mg of Sr^{2+} carrier ($Sr(NO_3)_2$), and 20 mg of Pb^{2+} carrier ($Pb(NO_3)_2$) for chemical recovery determination were added. The samples were evaporated to dryness with 3 × 20 mL 40% HF and 3 × 50 mL 65% HNO_3. The final residue was converted to nitrate form by evaporating 3 times with 10 mL of 65% HNO_3, dissolved in 70 mL of 1M HNO_3, and filtrated. If the chemical yield is determined using ICP-MS, an aliquot of 2.5 mL is taken for the analyses. The remaining solution was evaporated to dryness and dissolved in 10 mL of 1.5M HCl (3 times). This means that the sample was fully digested, which is necessary if one is interested in the total ^{210}Pb content of the soil sample. If only ^{90}Sr or the water-soluble (and bio-available) part of ^{210}Pb is of interest, leaching of the sample with 65% HNO_3 will be sufficient: ^{90}Sr soil values showed no differences when investigated after leaching or after full digestion.

Pb was separated on a Dowex 1 × 8 (100–200 mesh) column as described above for the bone samples.

With soil samples, the Sr fraction contains many more other ions compared to bone samples. Therefore, Sr must be preconcentrated by an additional precipitation step. The effluent from the Dowex column was evaporated to dryness and dissolved in 300 mL of 0.1M HNO_3; 10 g oxalic acid and 10 mL of 0.2M $Ca(NO_3)_2$ were added, the solution was heated to 90 °C, and the pH adjusted to 5.5–6 with ammonia solution. The Sr coprecipitated with calcium oxalate. Iron (both 2+, 3+) forms soluble complexes and remains in the solution. The precipitate was centrifuged and washed with 25 mL of double-distilled water 3 times. The oxalate precipitate was dissolved by evaporating with 65% HNO_3 (3 × 5 mL) and 2 mL of H_2O_2. The residue was taken up in 10–20 mL of 8M HNO_3. This solution was then loaded onto the SrSpec column. The procedure follows the one described above in "Purification of Sr by SrSpec Resin."

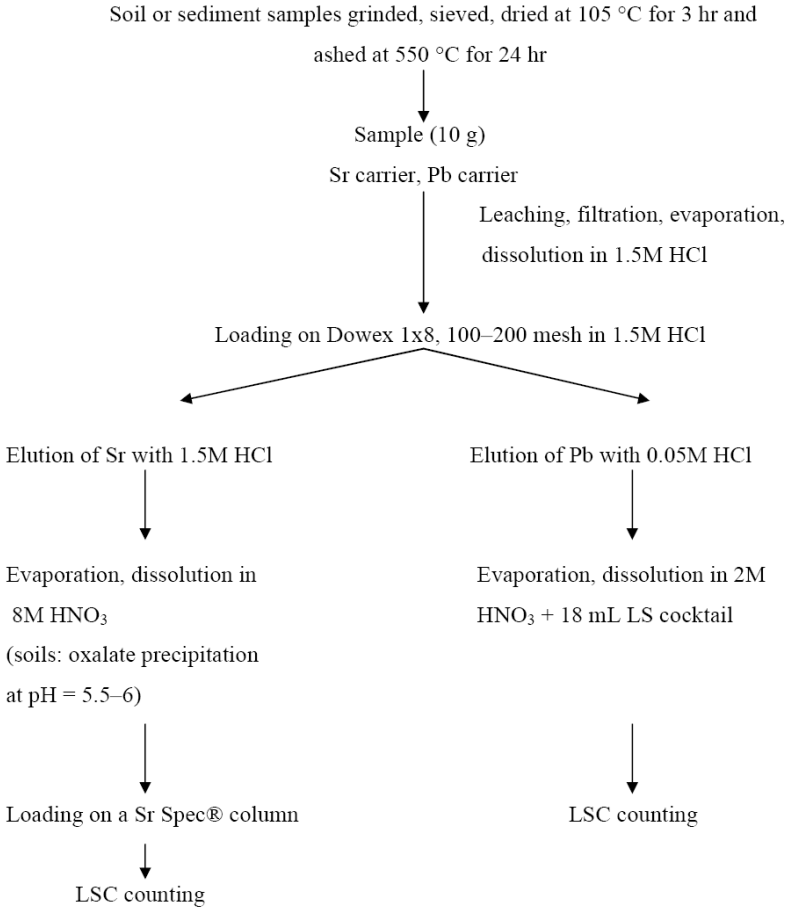


Figure 1 Flow chart of combined procedure for the determination of ^{90}Sr and ^{210}Pb in environmental samples.

RESULTS AND DISCUSSION

The applicability of our method for soil samples was shown by investigating IAEA soil-135 (Table 2) as well as a soil profile recently measured by Srncik et al. (2008) by using a different separation scheme and a gas proportional counter. The results obtained for the IAEA reference material agreed very well with the certified values corrected for the date of measurements (see Table 2).

Table 3 shows the data from the Naßfeld soil profile. This site is near Badgastein in the Alpine region of Salzburg, Austria. The 2 data sets from this work and from Srncik et al. (2008) generally agree very well within the 1-σ error; only the surface layer gave a slightly lower result in our measurements. The natural ^{210}Pb values of the fully digested soil layers exceed the anthropogenic ^{90}Sr values (the ^{90}Sr originates from Chernobyl; Srncik et al. 2008), at least in the uppermost layer, by 1 order of magnitude. In the deepest investigated layer (5.6–7.0 cm), they were of the same magnitude. This distinct decrease of ^{210}Pb with depth probably is due to its atmospheric origin: Naßfeld is situated quite near Radhausberg with its famous Badgastein radon healing gallery. The rocks there are known to be very porous, thus enabling the radon to escape easily from the ground into the atmosphere. Wet and dry deposition brings the long-lived radon progeny ^{210}Pb back to the soil surface. Preliminary results from other regions in Austria do not show such a distinct ^{210}Pb decrease with soil depth.

Table 2 Results obtained for analyzed reference material compared with certified values, corrected for the date of measurements (±1-σ error).

Name	Parameter	Measured	Certified value (95% confidence interval)
IAEA 135	^{90}Sr activity, Bq/kg dry mass	42.5 ± 0.3	43 (36 ÷ 53)
IAEA 135	^{210}Pb activity, Bq/kg dry mass	17.1 ± 0.2	13.4 (7.6 ÷ 20)

Table 3 Analysis results of ^{90}Sr and ^{210}Pb measurements of a soil profile from Naßfeld near Badgastein, Austria (reference date: May 1st, 1986); the given errors are 1-σ errors.

		^{90}Sr (Bq/kg)		^{210}Pb (Bq/kg)
Sample code	Depth (cm)	This work	Srncik et al. (2008)	This work
T9 G	0–1.1	108 ± 2	123 ± 2	1618 ± 12
T9 F	1.1–2.0	89.0 ± 2.5	93 ± 1	685 ± 4
T9 E	2.0–2.6	64.0 ± 1.2	67 ± 1	272 ± 2
T9 D	2.6–3.7	42.9 ± 1.4	47 ± 2	237 ± 2
T9 C	3.7–4.5	27.4 ± 1.4	32.9 ± 0.5	104 ± 1
T9 B	4.5–5.6	22.7 ± 1.4	25.4 ± 0.5	69 ± 1
T9 A	5.6–7.0	21.0 ± 1.4	24.2 ± 0.3	21 ± 1

CONCLUSIONS

With the presented 2-step procedure of lead separation on a Dowex followed by Sr purification on SrSpec, pure ^{210}Pb and ^{90}Sr spectra can be achieved by liquid scintillation counting of the respective elutions. An IAEA reference soil as well as a soil profile from an Alpine region (Naßfeld near Badgastein) was measured successfully by using the proposed procedure. The ^{210}Pb decrease with depth of the profile in this case is due to the atmospheric origin of this long-lived radon progeny.

ACKNOWLEDGMENTS

We thank Ing N Kandler for the ICP-MS measurements.

REFERENCES

Al-Merey R, Al-Shayah O. 2003. Ion exchange separation of lead from strontium in certified reference samples and spectrophotometric determination of lead as extractable ion-pair of $eosin^{2-}$ and the lead-cryptand $(2.2.2)^{2+}$ complex. *Journal of Trace and Microprobe Techniques* 21(1):13–24.

Alvarez A, Navarro N, Salvador S. 1995. New method for Sr-90 determination in liquid samples. *Journal of Radioanalytical and Nuclear Chemistry* 191(2):315–22.

Beighle DE, Boyazoglu PA, Hemken RW, Serumaga-Zake PA. 1994. Determination of calcium, phosphorus, and magnesium values in rib bones from clinically normal cattle. *American Journal of Veterinary Research* 55(1):85–9.

Brun S, Bessac S, Uridat D, Boursier B. 2002. Rapid method for the determination of radiostrontium in milk. *Journal of Radioanalytical and Nuclear Chemistry* 253(2):191–7.

D'Haese PC, Van Landeghem GF, Lambetrs LV, Bekaert VA, Schrooten I, De Broe ME. 1996. Measurement of strontium in serum, urine, bone, and soft tissues by Zeeman atomic absorption spectrometry. *Clinical Chemistry* 43(1):121–8.

Dietz ML, Horwitz EP, Nelson DN, Wahlgren M. 1991. An improved method for determining ^{89}Sr and ^{90}Sr in urine. *Health Physics* 61(6):871–7.

El Afifi EM, Borai EH. 2006. Performance characteristics of sequential separation and quantification of lead-210 and polonium-210 by ion exchange chromatography and nuclear spectrometric measurements. Hanford Site. *Journal of Environmental Quality* 35: 568–74.

Hardy EP, Meyer MW, Allen JS, Alexander LT. 1968. Strontium-90 on the earth's surface. *Nature* 219:584–7.

Horwitz EP, Dietz ML, Fisher DE. 1991. Separation and preconcentracion of Sr from biological, environmental and nuclear waste samples by extraction chromatography using a crown ether. *Analytical Chemistry* 63:522–5.

Horwitz EP, Chiarizia R, Dietz ML. 1992. A novel strontium-selective extraction chromatographic resin. *Solvent Extraction and Ion Exchange* 10(2):313–36.

Klevezal GA, Bakhur AE, Kalyakin VN, Krushinskaya NL. 2001. Dynamics of radionuclide concentrations in calcified tissues of reindeer in the western Russian Arctic. *Chemosphere* 42(1):61–7.

Landstetter C, Wallner G. 2006. Determination of strontium-90 in deer bones by liquid scintillation spectrometry after separation on Sr-specific ion exchange columns. *Journal of Environmental Radioactivity* 87: 315–24.

Michel H, Levent D, Barci V, Barci-Funel G, Hurel C. 2008. Soil and sediment analysis for the sequential determination of natural and anthropogenic radionuclides. *Talanta* 74:1527–33.

Mietelski JW, Gaca P, Zagrodzki P, Jasinska M, Zalewski M, Tomczak M, Vajda N, Dutkiewicz EM. 2001. ^{90}Sr and stable strontium in bones of wild, herbivorous animals from Poland. *Journal of Radioanalytical and Nuclear Chemistry* 247(2):363–70.

Seymour R, Sergent F, Knight K, Kyker B. 1992. Impact of sensitivity and throughput on optimum selection of a low-background alpha/beta gross counting system. *Radioactivity and Radiochemistry* 3:14–28.

Shabana EI, Al-Hussan KA, Al-Jaseem QK. 1996. Adaption of a radioanalytical method for strontium-90 to different kinds of environmental samples and its application for the investigation of some samples in the Riyad region. *Journal of Radioanalytical and Nuclear Chemistry* 212:229–40.

Srncik M, Hrnecek E, Steier P, Wallner A, Wallner G, Bossew P. 2008. The vertical distribution of ^{238}Pu, $^{239(40)}Pu$, ^{241}Am, ^{90}Sr and ^{137}Cs in Austrian soil profiles. *Radiochimica Acta* 96(9–11):733–8.

Staub JF, Foos E, Courtin B, Jochemsen R, Perault-Staub AM. 2003. A nonlinear compartmental model of Sr metabolism. Its physiological relevance for Ca Metabolism. *American Journal of Physics - Regulatory, Integrative and Comparative Physiology* 284:835–52.

Strandberg M, Strandgaard H. 1995. ^{90}Sr in antlers and bone of a Danish roe deer population. Hanford Site. *Journal of Environmental Radioactivity* 27(1):65–74.

Tatzber F, Irlweck K, Schaller F. 1982. Falloutradionuklide und natürliche Radioaktivität in Rehgewebeproben aus verschiedenen Gegenden Österreichs. Wien. Tierärztl. Mschr., 69. Jahrgang, Heft 3.

Taylor BTG, Moore JH, Hertelendy F. 1960. Variations in the mineral composition of individual bones of the skeleton of the domestic fowl. *British Journal of Nutrition* 14:49–57.

Tiller BL, Poston TM. 1999. Mule deer antlers as biomonitors of strontium-90 on the Hanford Site. *Journal of Environmental Radioactivity* 47(1):29–44.

Vajda N, Ghods-Esphahani A, Cooper E, Danesi PR. 1992. Determination of radiostrontium in soil samples using a crown ether. *Journal of Radioanalytical and Nuclear Chemistry* 162(2):307–23.

Vrcek P, Benedik L, Pihlar B. 2004. Determination of ^{210}Pb and ^{210}Po in sediment and soil leachates and in biological materials using a Sr-resin column and evaluation of column reuse. *Applied Radiation and Isotopes* 60(5):717–23.

Wallner G. 2002. Determination of Ra-228, Ra-226 and Pb-210 in drinking water using liquid scintillation counting. In: Möbius S, Noakes JE, Schönhofer F, editors. *LSC 2001, Advances in Liquid Scintillation Spectrometry 2001*. Tucson: Radiocarbon. p 269–74.

2.2 Determination of ^{90}Sr and ^{210}Pb in deer bone samples by liquid scintillation counting after ion-exchange procedures

Wallova G, Kandler N, Wallner G (2010) J Radioanal Nucl Chem 286:429-433

J Radioanal Nucl Chem (2010) 286:429–433
DOI 10.1007/s10967-010-0725-z

Determination of ^{90}Sr and ^{210}Pb in deer bone samples by liquid scintillation counting after ion-exchange procedures

Gabriela Wallova · Norbert Kandler · Gabriele Wallner

Received: 14 July 2010 / Published online: 19 August 2010

Abstract This work describes a procedure for the isolation of ^{90}Sr and ^{210}Pb from deer bones by anion exchange methods and their sequential measurement by LSC. To prevent collection of Pb on the Sr·Spec® resin we first separated Pb on a Dowex anion exchange column. Sr, which is not held back on the Dowex column, was then purified using Sr·Spec® resin: first Ca and the Ra isotopes were eluted with 3 M HNO_3 and then Sr was eluted with distilled water. With this 2-steps procedure pure ^{210}Pb and ^{90}Sr spectra can be achieved. The chemical yield of both steps was determined by ICP-MS. Our ^{90}Sr results show satisfying agreement with data obtained by a shorter Sr·Spec® method and also by the "classical" ^{90}Sr determination using fuming nitric acid. Also ^{210}Pb results were checked by re-measuring bone samples with already known ^{210}Pb activities. Further our method was verified on the reference sample IAEA-A-12.

Keywords Liquid scintillation counting · ^{90}Sr · ^{210}Pb · Bone samples · Sr·Spec® resin · Anion exchange

Introduction

The fission product ^{90}Sr ($T_{1/2}$ = 28.7 years) can be found in the environment due to the global fallout from atmospheric nuclear explosions and the Chernobyl accident in1986. When dispersed, ^{90}Sr migrates, sorbs onto natural matrices and also integrates in the food chain [1]. It has high ecological importance, because as a homologue to Ca it accumulates in bone tissues. ^{210}Pb is a naturally occurring radionuclide which also accumulates in bones. The presence of large amounts of ^{90}Sr and ^{210}Pb in living organisms can lead to somatic as well as genetic changes and for this reason their monitoring in the environment is very important [2–7]. Deer bone samples were selected as a feasible environmental contamination indicator for these natural and anthropogenic activity concentrations. The animals were not hunted for research, but to maintain the ecological equilibrium in nature.

As a pure β-emitter, ^{90}Sr ($E_{\beta,\max}$ = 546 keV) can only be determined after separation from interfering radionuclides. In recent years an extraction-chromatographic method using Sr·Spec® resin for the determination of ^{90}Sr in environmental samples was introduced in many laboratories [8–10]. The Sr·Spec® resin specifically holds back Sr ions and allows a rapid and simple separation of strontium from potassium, calcium and many other elements. Sr is eluted from the column with diluted HNO_3 or with water.

However, this extraction-chromatographic method does not eliminate ^{210}Pb also present in most samples and so often ^{210}Pb interfered with the ^{90}Sr LSC spectrum [2]. In order to avoid this interference, precipitations steps were suggested before adding the sample to the Sr·Spec® resin [11]. We tried to circumvent this time consuming procedure by an additional ion-exchange step; this method had been tested with an artificial "bone standard solution" and was published previously [12].

To prevent the collection of Pb on the Sr·Spec® resin, we first separated Pb on a Dowex 1 × 8 (100–200 mesh) anion exchange column. Sr, which is not retained on the column, was then purified using Sr·Spec® resin. The chemical yields for the respective separations were determinated using ICP-MS. Our results show satisfying agreement with data

G. Wallova (✉) · N. Kandler · G. Wallner
Institut für Anorganische Chemie, Universität Wien, Währinger Straße 42, 1090 Wien, Austria
e-mail: gabriela.wallova@univie.ac.at

obtained by a shorter Sr·Spec® method and also by the "classical" ^{90}Sr determination using fuming nitric acid [13]. Also ^{210}Pb results were checked by re-measuring bone samples with ^{210}Pb concentrations already determined via ^{210}Po [13]. Further our method was validated on the reference sample IAEA-A-12.

Experimental

Reagents and equipment

All reagents were of analytical grade: 65% HNO_3, 37% HCl, purchased from Merck. The liquid scintillation cocktail Optiphase HiSafe^{TM}III, purchased from Perkin Elmer. 1-octanol, $SrNO_3$, $PbNO_3$ purchased from Fluka. Analytical grade ion exchange resin: Dowex 1 × 8 (Cl^--form, 100–200 mesh) from Fluka, Sr·Spec Resin (100–150 µm) from Eichrom, USA.

The dilutions were made with deionized Milli-Q 18 MΩ·cm water (Millipore, USA).

Equipment used: ICP-MS Agilent 7500ce, Waldbronn, Germany, equipped with a CETAC ASX-520 autosampler; LS counter Quantulus 1220, WallacOy, Finland (now Perkin-Elmer).

Separation methods

This separation method was previously tested for a "bone standard solution" containing various cations in 0.5 M HBr and 1.5 M HCl, respectively, and for the soil reference sample IAEA-135; soil samples of known ^{90}Sr content had been re-measured for method validation [12]. While the bone standard solution was prepared to simulate the mineral composition of bones, in this work the method was applied for real bone samples.

The bones were stored deep-frozen and then ashed for 17–22 h at 450 °C. After grinding and weighing 1 g of bone ash was dissolved in 5 mL of 8 M HNO_3, 2.5 mg of Sr^{2+} carrier (as strontium nitrate) and 10 mg of Pb^{2+} carrier (as lead nitrate) were added for chemical yield determination. The solution was boiled under reflux for 3 h, filtrated, and evaporated to dry. The residue was dissolved in 10 mL of 1.5 M HCl and loaded on a Dowex 1 × 8 (100–200 mesh, Cl^- form) column (1 cm inner diameter, 20 cm length and 0.008 L bed volume) for Pb separation.

The column was rinsed with 50 mL of 1.5 M HCl. This rinsing solution contains Sr^{2+} and all other cations (also ^{210}Bi, ^{210}Po) with the exception of Pb^{2+}. Subsequently the column was washed with 70 mL of 0.05 M HCl to elute Pb^{2+}. Both solutions were evaporated to dryness. The residue containing Pb^{2+} was dissolved in 1.5 mL of 2 M HNO_3 and 6.75 mL of water. From this solution 0.25 mL were collected for ICP-MS analysis, and 8 mL were mixed with 12 mL of liquid scintillation cocktail HiSafe^{TM}III and measured by LSC.

The chemical blank value in the ^{210}Pb region was 1.38 cpm. With a counting time of 1,000 min, the lower limit of detection (LLD) calculated by the [14] was 6.7 Bq/kg ^{210}Pb (a chemical yield of 44% and the sample mass of 1 g were assumed).

The residue containing Sr^{2+} and other cations was dissolved in 10 mL of 8 M HNO_3 and was loaded onto a Sr·Spec® column (3 g of resin), rinsed with 100 mL of distilled water saturated with n-octanol, and 10 mL of 8 M HNO_3 (saturated with n-octanol) for further Sr purification. The column was consequently rinsed with 5 mL of 8 M HNO_3 (removal of Bi and Po) and 10 mL 3 M HNO_3 (removal of Y, Ra and Ca). Strontium was stripped with 8.25 mL distilled water. From this rinsing solution 0.25 mL were collected for ICP-MS measurement, and 8 mL were mixed with 12 mL HiSafe^{TM}III cocktail and measured by LSC (Fig. 1).

The chemical blank value in the ^{90}Sr region was 3.15 cpm. With a counting time of 1,000 min the LLD calculated by the [14] was 5.5 Bq/kg ^{90}Sr (a chemical yield of 80% and the sample mass of 1 g were assumed).

If ^{90}Sr is the only nuclide of interest, it is possible to use only step 2 of the above given procedure (the Sr·Spec® step). The dissolved sample is directly loaded onto the Sr·Spec® resin (Fig. 1, fraction A).

However, in this case a contamination of the ^{90}Sr with interfering ^{210}Pb cannot be excluded because the latter is also extracted on the Sr·Spec® column [2]. We found out that re-using the column less than 6 times reduces this problem considerably. Only when samples with high ^{210}Pb activity in comparison with ^{90}Sr activity are analyzed, previous lead separation is necessary.

For data comparison our bone samples and also the IAEA-A-12 reference material for ^{90}Sr were investigated using both procedures. The ^{90}Sr and ^{210}Pb activity concentrations of two samples (sample code 134 and 127) were compared with old results gained by the "classical" ^{90}Sr separation using fuming nitric acid and the "classical" ^{210}Pb determination via ^{210}Po [13].

Results and discussion

Table 1 shows our ^{90}Sr results for the reference material IAEA-A-12 (animal bone) obtained by the two methods described in this work (2 step-procedure and Sr·Spec® only); both results are within the 95% confidence interval of the certified value.

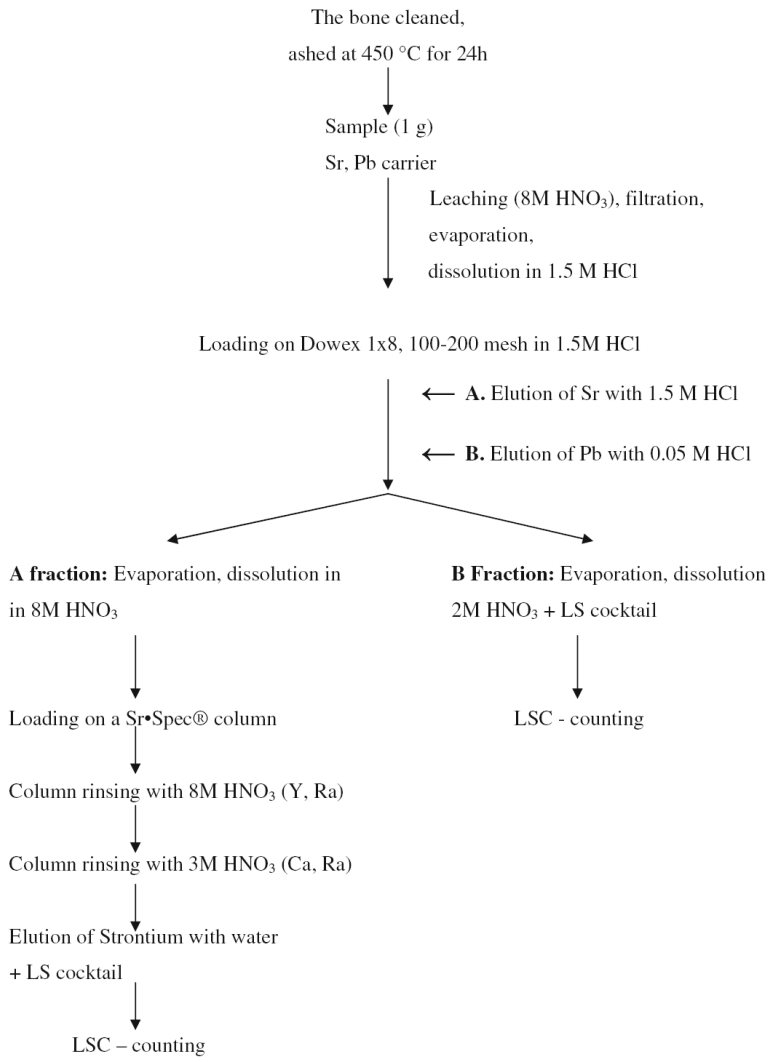


Fig. 1 The two-steps procedure of lead separation using Dowex 1 × 8 (100–200 mesh) followed by Sr purification on Sr·Spec

Table 1 Activities of ^{90}Sr for reference material IAEA-A-12 (animal bone) obtained using two different procedures, corrected for the date of measurements (±1σ error)

Name	Parameter	Measured after two-steps procedure	Measured after modified Sr·Spec procedure	Certified value (95% confidence interval)
IAEA-A-12	^{90}Sr activity, Bq/kg dry mass	29.8 ± 1.8	30.9 ± 2.1	27.7 (19.2–32.1)

We also re-measured two reindeer bone samples and found excellent agreement with the old data gained by the "classical" methods (^{90}Sr separation using fuming nitric acid, and ^{210}Pb determination via ^{210}Po, see Table 2).

Table 3 shows our deer bone results from animals hunted in different regions of Austria obtained by the two-steps procedure (^{90}Sr and ^{210}Pb) and also by the faster Sr·Spec® method (^{90}Sr only).

In most cases there was good correspondence between the methods, only a few samples gave differing results. A check of the 2 spectra with too high results with the Sr·Spec® only method revealed neither ^{210}Pb or ^{210}Bi

Table 2 Comparison of the activities of ^{90}Sr and ^{210}Pb in bone samples measured by different methods, reference date: 1st January 2010 (±1σ-uncertainties)

Element:	^{90}Sr	^{90}Sr	^{90}Sr	^{210}Pb	^{210}Pb
Method:	2-steps method *A* (Bq/kg)	Sr·Spec method *A* (Bq/kg)	Fumic nitric acid method *A* (Bq/kg)	2-steps method *A* (Bq/kg)	Determination via ^{210}Po *A* (Bq/kg)
Sample code: 134	206 ± 16	212 ± 19	207 ± 7	126 ± 10	125 ± 5
Sample code: 127	171 ± 11	178 ± 12	173 ± 6	34 ± 5	33 ± 2

Table 3 Activities of ^{90}Sr and ^{90}Pb in bone samples measured by the two methods

Description of the sample			^{90}Sr two-step method		^{90}S Sr·Spec method		^{210}Pb two-step method	
Hunting place	Age	Hunting date	*A* (Bq/kg) ± 1σ	*Y* (%)	*A* (Bq/kg) ± 1σ	*Y* (%)	*A* (Bq/kg) ± 1σ	*Y* (%)
Neulengbach	11 month	12.04.2002	55.1 ± 5.1	66.7	51.9 ± 4.4	80.8	18.5 ± 2.6	56.6
Neuwaldegg	6 year	11.01.2002	54.1 ± 4.9	56.9	107.9 ± 8.9	70.1	11.1 ± 3.3	30.1
Nickelsdorf	8–9 year	02.07.2001	26.8 ± 3.3	73.7	24.7 ± 4.1	66.3	8.2 ± 2.7	35.7
Mirnock	6 year	06.07.2006	200.1 ± 12.6	66.6	202.2 ± 14.8	83.6	36.5 ± 3.5	58.9
Mariapfarr	Unknown	03.09.2006	283.9 ± 16.2	84.5	223.9 ± 14.5	95.2	48.7 ± 4.4	51.5
Treffning	Unknown	10.12.2007	57.6 ± 5.1	80.9	98.1 ± 6.4	85.6	32.9 ± 4.9	29.0
St. Michael	7–8 year	22.12.2007	66.7 ± 5.3	97.8	67.3 ± 6.4	98.9	20.1 ± 4.1	32.5
Lobau	5 year	20.03.2002	189.1 ± 11.5	71.2	193.8 ± 11.1	88.9	95.5 ± 8.1	66.1
Kaprun West	10 month	21.12.2009	128.3 ± 9.9	86.3	130.5 ± 10.1	96.0	18.3 ± 3.7	55.3
Melk	Unknown	22.12.2009	71.7 ± 7.3	75.7	76.8 ± 7.6	84.1	16.1 ± 5.3	25.0

The activities are corrected for the hunting date and furnished with 1σ-uncertainties

contamination. Both spectra were confirmed as a pure ^{90}Sr spectra due to the ingrowing daughter nuclide ^{90}Y, so a reason for the observed differences.

However, the short Sr·Spec® method only is insufficient to eliminate ^{210}Pb occurring in the sample in excess compared to ^{90}Sr. Therefore we prefer to avoid the ^{210}Pb loading onto the column, together with Sr. We applied the Dowex separation step to obtain a pure Pb in one fraction.

Conclusions

The two-steps procedure for ^{90}Sr and ^{210}Pb determination as well as the faster Sr·Spec® method (for ^{90}Sr determination only) were validated by the reference material IAEA-A-12 (animal bone) and by re-measuring samples with well known ^{90}Sr and ^{210}Pb content. Both methods were then applied to deer bone samples from different regions in Austria. Also here the results generally agreed well. Although the Sr·Spec® method is much faster we strongly favourite the two-steps procedure: here also information about the sample's ^{210}Pb concentration is gained, and the ^{90}Sr fraction is free of any ^{210}Pb contamination. Especially if ^{210}Pb is in excess compared to ^{90}Sr, the Pb separation before the Sr purification is a prerequisite for an undisturbed ^{90}Sr spectrum.

Acknowledgments We thank all institutions who provided us with deer bone samples.

References

1. Yamagata N, Matsuda S, Chiba M (1969) Radioecology of cesium-137 and strontium-90 in a forest. J Radiat Res 10:107–112
2. Landstetter C, Wallner G (2006) Determination of strontium-90 in deer bones by liquid scintillation spectrometry after separation on Sr-specific ion exchange columns. J Environ Radioact 87:315–324
3. Mietelski JW, Gaca P, Zagrodzki P, Jasinska M, Zalewski M, Tomczak M, Vajda N, Dutkiewicz EM (2001) ^{90}Sr and stable strontium in bones of wild, herbivorous animals from Poland. J Radioanal Nucl Chem 247:363–370
4. Shabana EI, Al-Hussan KA, Al-Jaseem QK (1996) Adaption of a radioanalytical method for strontium-90 to different kinds of environmental samples and its application for the investigation of some samples in the Riyadh region. J Radioanal Nucl Chem Lett 212:229–240
5. Galambos M, Kufcakova J, Rajec P (2009) Sorption of strontium on Slovak bentonites. J Radioanal Nucl Chem 281:347–357
6. Bem H, Bakir YY, Shuker SM (1991) A rapid method for the determination of strontium-90 in powdered milk. J Radioanal Nucl Chem 147:263–268
7. Berlizov AN, Sajeniouk AD, Tryshyn VV (2005) A technique for the determination of ^{90}Sr, plutonium and americium isotopes in environmental samples. J Radioanal Nucl Chem 263:307–310
8. Vajda N, Ghods-Esphahani A, Cooper E, Danesi PR (1992) Determination of radiostrontium in soil samples using a crown ether. J Radioanal Nucl Chem Articles 162:307–323

9. Horwitz EP, Dietz ML, Fisher DE (1991) Separation and preconcentration of strontium from biological, environmental, and nuclear waste samples by extraction chromatography using a crown ether. Anal Chem 63:522–525
10. Alvarez A, Navarro N, Salvador S (1995) New method for ^{90}Sr determination in liquid samples. J Radioanal Nucl Chem Articles 191:315–322
11. Saxén R (2002) Determination of ^{90}Sr by extraction chromatography in the presence on ^{210}Pb in environmental samples. In: Möbius S, Noakes J, Schönhofer F (eds) LSC 2001, advansec in liquid scintillation spectrometry. Radiocarbon, Tuscon, p 389
12. Wallova G, Wallner G (2009) Isolation and measurement of strontium-90 and lead-210 in environmental samples using lsc. In: Eikenberg J, Jäggi M, Beer H, Baehrle H (eds) International conference on advances in liquid scintillation spectrometry 2008. Radiocarbon, Tuscon, Davos, Switzerland, p 367
13. Bossew P, Ichikawa M, Mraz G, Wallner G, Wenish A (2000) Radiological investigations in the surroundins of Bilibino, Chukotka, Russia. J Environ Radioact 51:299–319
14. Seymour R, Sergent F, Knight K, Kyker B (1992) Impact of sensitivity and throughput on optimum selection of a low-background alpha/beta gross counting system. Radioact Radiochem 3:14–28

2.3 Monitoring of radionuclides in soil and bone samples from Austria

Wallova G, Kandler N, Wallner G (May, 2011) manuscript submited to J Environment Radioact

MONITORING OF RADIONUCLIDES IN SOIL AND BONE SAMPLES FROM AUSTRIA

Gabriela Wallova*, Norbert Kandler, Gabriele Wallner
Institut für Anorganische Chemie, Universität Wien, Währinger Str. 42,
A-1090 Vienna, Austria

*Corresponding author: Gabriela Wallova, Department of Inorganic Chemistry, University of Vienna, Währinger Straße 42, A-1090 Vienna, Austria
Tel.: +43-1-4277-52624
Fax: +43-1-4277-52620
e-mail: gabriela.wallova@univie.ac.at

Abstract

The activity concentrations of anthropogenic (^{90}Sr, ^{137}Cs) and natural (^{238}U, ^{232}Th, ^{40}K, ^{210}Pb) radionuclides were determined in soil samples from three different regions in Austria (Styria, Carinthia and Salzburg). A direct correlation between the activity concentration of ^{90}Sr and ^{137}Cs in soil samples and site altitude was found. ^{90}Sr and ^{210}Pb activity concentrations were also determined in bones ash of deer hunted in these regions. Additional bone samples were collected all over Austria. The ^{90}Sr values in deer bones are directly proportional to the values in the respective soil samples and also to the age of the animals.

For the ^{90}Sr and ^{210}Pb determinations in bone samples first Pb was separated on a Dowex column, then Sr was purified using Sr•Spec® resin. In soil samples an additional hydroxide precipitation was employed to eliminate interfering iron. For the first time also the 3M Empore® Sr Rad disk method was successfully applied to bone samples. With this method the chemical procedure can be shortened by more than a factor of 2. The ^{90}Sr and ^{210}Pb fractions were measured by liquid scintillation counting, while the chemical

yields were determined by ICP-MS. The activity concentrations of ^{40}K, ^{238}U, ^{232}Th and ^{137}Cs in soil samples were evaluated using gamma spectrometry.

Key words Natural radionuclides · Anthropogenic radionuclides · Environmental samples · Sr•Spec® resin · 3M Empore™ Sr Rad Disk

Introduction

Naturally occurring radionuclides like ^{40}K and the members of the uranium and thorium decay chains are omnipresent in the environment and their distribution in soil profiles has been studied by several authors [1-4]. Since the atomic weapons tests in the fifties and early sixties of the last century and the Chernobyl accident in 1986, also anthropogenic fission and activation products are dispersed in nature. Due to their relatively long half-lifes of 28.5 and 30.17 yr, the fission products ^{90}Sr and ^{137}Cs which are of relevance from the radiation protection point of view, can still be detected in environmental samples. In this paper we present soil sample data of natural and anthropogenic radionuclides from selected areas in Austria. The measured activity concentrations of the artificial nuclides increased with increasing altitude of the sampling sites due to higher amount of precipitation in the mountains, which is the main scavenging process for airborne particles [5, 6]. From the ^{90}Sr/^{137}Cs activity ratio measured the portions of the respective contamination sources could be determined [7]. The obtained data set a baseline for future changes in environmental radioactivity coupled with human activities [3].

The main emphasis of our work, however, was the investigation of animal bones with respect to the β-emitter ^{90}Sr which is a bone seeker due to its chemical similarity with calcium [8]. In the past several papers about ^{90}Sr in deer and roe deer of Austrian origin were published [6, 9, 10]. To have also more recent data, additional to soil profiles also bone samples from deer were collected and their ^{90}Sr and ^{210}Pb concentrations were measured. The animals stem from sites with altitudes between 150 and 1530 m a.s.l. and these recent data should fill a gap in the already published values. The latter

were mostly from animals from lower parts of Austria, only one site was an Alpine one. On the other hand, by comparing old and recent data possible changes in the bioavailability of ^{90}Sr could be detected. Problems addressed already in the preceding papers as e.g. ^{90}Sr concentration in dependence of animal age or site altitude could now be investigated in more detail.

For the determination of ^{90}Sr in environmental samples numerous methods such as fuming nitric acid procedure, precipitations, ion exchange, or extraction techniques using Sr•Spec® resin from Eichrom Technologies have been described [11-14]. The most convenient method for determination of ^{90}Sr – at least in aqueous samples - utilizes a strontium selective ion exchange material in filter form, namely the Empore™ Strontium Rad Disk [15-18]. In this work, we successfully applied the Sr Rad Disk method for determination of ^{90}Sr in bone ash samples and verified the results by comparing the results with data gained by using the Sr•Spec® technique. The measurement of the ^{90}Sr and of the previously separated ^{210}Pb was done by low-level liquid scintillation counting.

Experimental

Reagents and equipment

All reagents were of analytical grade: Hydrochloric acid 37%, Nitric acid 65%, Methanol 99.9%, Oxalic acid dihydrate, Natrium hydroxide, aqueous Ammonia solution 25%, Hydrogen peroxide 30% solution purchased from Merck; Ethylenediaminetetraacetic acid disodium salt dihydrate 99.0-101% purchased from Sigma; liquid scintillation cocktail OptiPhase HiSafe™III from Perkin Elmer; Empore™ Sr RAD disks from 3M Company; strontium nitrate, lead nitrate, Dowex 1x8 (Cl^-- form, 100-200 mesh) from Fluka.

The dilutions were made with deionized Milli-Q 18 MΩ•cm water (Millipore, USA).

Chemical yield for strontium and lead separations were determined with ICP-MS Agilent 7500ce Instrument, equipped with a CETAC ASX-520 autosampler from Waldbronn, Germany. Activity concentrations of ^{90}Sr and ^{210}Pb were conducted on LS counter Quantulus 1220 from WallacOy, Finland (now Perkin-Elmer). Reverse electrode Germanium Detector Canberra GR 2020 was used for the activity concentration determinations of ^{137}Cs and ^{238}U and ^{232}Th.

Collection of the samples

Our soil samples stem from the eastern part of the Alps in Styria (Rettenegg, 860 m; Kaltenegg, 1000 m), the southern part of the Central Alps in Carinthia (Ossiacher Tauern, 680 m; and Saualpe, 1895 m; a mountain ridge with Mirniger Alm, 1530 m, on its western slope) and from the Central Alps in Salzburg (Mariapfarr region, 1340 m; 1530 m and 1786 m). With a tube an approximately 10 cm deep bore was drilled into the soil. The obtained samples were divided into layers. Before measurement the samples were air dried.

The bones of deer hunted in different regions in Austria were obtained from institutions and private hunters. The bones were stored deep frozen.

Gamma spectrometry of soil samples

The air dried soil samples were cleaned by removing big stones and plant roots, grinded and sealed in plastic Marinelli beakers. The Marinelli beakers were filled to a certain height, so that the geometry was the same for all samples. The respective sample mass was about 10 g. Samples were stored for 1 month before measurement to achieve ingrowth of Rn isotopes with their respective daughters. The activity concentrations of anthropogenic ^{137}Cs and natural ^{40}K, ^{238}U and ^{232}Th in soil samples were evaluated using a Reverse Electrode Ge Detector (Canberra GR 2020) with 20% efficiency relative to NaI and 3 keV resolution. As previously published in our work, the respective

specific activities (Bq.kg^{-1}) of ^{238}U and ^{232}Th were determined indirectly using the daughters ^{226}Ra, ^{214}Pb, ^{214}Bi and ^{228}Ac, ^{212}Pb, ^{208}Tl, respectively [19]. The activity concentrations of ^{40}K and ^{137}Cs were calculated directly using the gamma lines at 1460.8 keV and 661.6 keV, respectively.

The determination of ^{90}Sr and ^{210}Pb in soil and bone samples

The bone ash samples were treated according to our two-steps procedure which is given in more detail in [20, 21]. In the first step, Pb was separated from Sr and other cations on a Dowex 1x8 (100-200 mesh) column. Subsequently ^{90}Sr was purified on Sr•Spec® resin. Both fractions were mixed with the cocktail OptiPhase HiSafe™III and measured by LSC on a Quantulus®1220 (Wallac, Finland, now Perkin Elmer). The lower limit of detection (LLD) of ^{90}Sr was calculated according to [22]. It was 6.5 Bq.kg^{-1} for bone ash samples (sample counting time: 200 min, background counting time: 1000 min, the mean value for chemical recovery: 69% and sample mass: 1g of bone ash), and 0.6 Bq.kg^{-1} for soil samples (counting times and chemical recovery as with ash samples, sample mass: 10g of air dried soil). The LLD of ^{210}Pb calculated by the [22] was 6 Bq.kg^{-1} for bone samples (counting times as given above, chemical recovery: 51% and sample mass: 1g of bone ash), and 0.8 Bq.kg^{-1} for soil samples (chemical recovery: 41% and sample mass: 10g of air dried soil).

For soil samples, the two-step procedure was extended by alkaline precipitation of iron as described in literature [23-25]. After the Pb separation on Dowex, the Sr containing fraction was evaporated to dryness. The residue was taken up in approximately 50 mL water and spiked with 5 mg Fe^{3+} carrier. While stirring, 6M NaOH was added until pH=9 was reached. The solution was heated to 70℃ and stirred for 30 minutes. After cooling, the iron hydroxide precipitate was centrifuged off. To the supernatant 50 mg of Ca^{2+} carrier and 10 g of oxalic acid were added. The pH was adjusted to 5 - 6 with aqueous ammonia and the suspension was heated to 70℃ while stirring for 30 minutes. After cooling the suspension was centrifuged. The precipitate was dissolved in a minimal amount of concentrated nitric acid and water was

added to obtain 8M dilution. Sr was separated from this solution with Sr-Spec® resin according to our two-step procedure [20, 21].

The determination of ^{90}Sr in bone samples using Empore^{TM} Sr RAD disks

As for the Sr•Spec procedure, 1 g of bone ash was dissolved in 10 mL of 8M HNO_3 and 1 mg of Sr^{2+} (strontium nitrate) and 5 mg of Fe^{3+} carrier was added for chemical yield determination. The solution was refluxed for 3 hours, cooled, filtrated and evaporated to near dryness. Further sodium hydroxide and oxalic acid treatment is the same as described above for soil samples (sodium hydroxide treatment at pH=9 was applied to precipitate Pb^{2+} [26]). Finally, the 8M HNO_3 solution was further diluted with water to achieve 2M HNO_3 concentration.

The 3M Empore Sr RAD disk was washed with 2mL of methanol and conditioned with 20 mL 2M HNO_3. The 2M HNO_3 sample solution was passed through the disk with a flow rate of less than 10 mL/min using a slight vacuum. After that the disk was rinsed with 20 mL of 2M nitric acid to remove Y^{3+}. The disk was rinsed with 2 mL of 0.5M Na_2EDTA (fraction discarded) and ^{90}Sr was eluted from the disk using 8.25 mL of 0.5M Na_2EDTA (pH=9-11). From this total 8.25 mL Sr-fraction, 0.25 mL were taken for determination of chemical yield by ICP-MS. The remaining 8 mL of the sample were mixed with 12 mL of liquid scintillation cocktail OptiPhase HiSafe™III and measured by LSC. During the whole filtration procedure air was not allowed to pass through the filter in order to prevent radon daughter entrapment on the disk [16]. The LLD for^{90}Sr calculated according [22] was the same as for the two-steps procedure (6 $Bq.kg^{-1}$ bone ash).

The described procedure was verified using IAEA A-12, a bone ash reference sample.

Results and Discussion

In soil samples the specific activities of ^{232}Th and ^{238}U were calculated through its daughter radionuclides (^{228}Ac, ^{212}Pb and ^{208}Tl) and (^{214}Pb, ^{214}Bi and ^{226}Ra) respectively. The world-wide median values published by UNSCEAR are 400, 35 and 30 Bq.kg^{-1} for ^{40}K, ^{238}U and ^{232}Th, respectively [27]. The specific activities of soils studied in this work are comparable to these median values: they lie in the range of 230-709 Bq.kg^{-1} for ^{40}K, 15-45 Bq.kg^{-1} for ^{238}U and 30-46 Bq.kg^{-1} for ^{232}Th.

The main emphasis of our work was the determination of the activity concentrations of ^{90}Sr and ^{137}Cs in soil samples and of ^{90}Sr in bones. The data of these anthropogenic nuclides were compared to the activity concentration of the naturally occurring ^{210}Pb.

Table 1 shows the soil results for the three nuclides of interest together with the ^{90}Sr/^{137}Cs ratio which can be used to identify the source of the contamination: for global fallout the ratio is 0.64 [27] (calculated for 2005), while for contaminations from the Chernobyl accident the values are between 0.040 and 0.045. After the Chernobyl accident ^{90}Sr/^{137}Cs ratios in air filters from Austria were in the range 0.004 - 0.050 [28], in Munich a value of 0.009 was found [29]. Experimental data indicate the ^{90}Sr/^{137}Cs ratio in soils being two times higher than in air filters [28], as the Chernobyl ratio is superimposed by the omnipresent higher global fallout ratio. In the struck regions of Austria the deposition of ^{90}Sr from Chernobyl fallout was reported to be in the same range as the ^{90}Sr deposition still present from the nuclear bomb testing [5, 30, 31].

The activity levels of the global fallout nuclides show a correlation with the site altitude, as the nuclides are mainly washed out by wet precipitation, which is higher in the mountains. Principally the same is true for the deposition of Chernobyl fallout, but the regional variations are much larger in this case, as precipitation occurred only in some regions during the critical time-span when the radioactive cloud passed Austria.

All soil samples were taken from undisturbed pasture-land. From each sample site 4 cores were taken within a distance of a few meters and mixed well. It is well known from the literature that small scale variations of deposited activities up to a factor of 3 can be found [32, 33]. In all samples the maximum values for ^{90}Sr and ^{137}Cs were measured in the uppermost 4 cm of the core. The highest values were found on the Saualpe / Mirniger Alm with about 2000 Bq.kg^{-1} ^{137}Cs and 160 Bq.kg^{-1} ^{90}Sr. On this mountain ridge rain was reported during the days after the Chernobyl accident. The corresponding ^{90}Sr/^{137}Cs ratio is 0.08-0.09, also clearly indicating a large contribution from Chernobyl (91-94%). On the other hand the lowest ^{90}Sr and ^{137}Cs values were measured in Kaltenegg (8 and 77 Bq.kg^{-1}, respectively, with a ratio of 0.1); a few kilometers apart in Rettenegg the respective data were higher with a lower ^{90}Sr/^{137}Cs ratio (0.05) indicating again a higher contribution from Chernobyl (96%), probably due to local rainfall. The samples from Mariapfarr generally showed lower activity levels in the surface layers together with clearly higher ^{90}Sr/^{137}Cs ratios. Here the portion of nuclides from the global fallout is higher (54%) as after the Chernobyl accident the weather was dry. The Mariapfarr sampling sites were all on the southern slope of one specific mountain ridge in the Niedere Tauern, showing very clearly the site altitude dependence of the activity concentrations (see Fig. 1). Another activity / site altitude correspondence (with comparably higher activity concentrations) can be found for the sites in Carinthia with higher contributions from Chernobyl.

^{210}Pb, on the contrary, is a naturally occurring radionuclide and its content in soil depends on the bedrock from which the soil had been built up by weathering. All the samples stem from gneiss areas, therefore the variation of the activity concentrations is rather low (30-100 Bq.kg^{-1}).

^{90}Sr and ^{210}Pb activity concentrations were also measured in deer bone samples from various regions of Austria (see Tab. 2). Some values were adopted from earlier publications to give an overview of samples collected from sites covering a broad range of altitudes [6, 21]. Deer usually graze larger areas and therefore small scale variations of deposited ^{90}Sr should be ruled out. Animals were collected from the sites where soil samples were available but also additional regions were investigated.

Two different methods were used for ^{90}Sr determination (two steps method using Dowex for ^{210}Pb separation and Sr purification with Sr Spec resin; and using 3M Empore Sr disk after removing of ^{210}Pb by $Fe(OH)_3$ co-precipitation). The data obtained from both methods were in good agreement (see Table 3). The Sr disks originally were developed for determination of ^{90}Sr in liquid samples. In this work we successfully verified the applicability of this tool for the determination of ^{90}Sr in bone samples using reference sample IAEA-A-12 (certified value: 27.7 Bq.kg^{-1}, 95% confidence interval: (19.2-32.1 Bq.kg^{-1}) (Table 3). Using Sr disks reduced the chemical processing time for bone ash samples by more than a factor 2, since the separation step by “filtration” is much faster than by using a Sr-Spec column.

In the recent investigation the highest ^{90}Sr level was found in an animal from Mariapfarr (248 ± 17 Bq.kg^{-1}ash, 1350 m a. s. l.) and the lowest value was observed in a sample from Petronell (18 ± 3 Bq.kg^{-1}ash, 175 m a. s. l.) (^{210}Pb levels in bone ash vary from 7 ± 2 Bq.kg^{-1} to 54 ± 6 Bq.kg^{-1}). This corresponds to 114 and 9 Bq.kg^{-1} bone sample. In 2001-2002 ^{90}Sr contents from global weapons fallout and from Chernobyl fallout up to 117 Bq.kg^{-1} of animal bones were reported for site altitudes up to 427 m a.s.l. and about 400 Bq.kg^{-1} for Kaunertal (1700 m a.s.l.) [6], with a big gap for altitudes between 500 and 1500 m a.s.l. Our recent data are clearly lower than the old ones, probably indicating that the bioavailability of ^{90}Sr had decreased.

^{90}Sr activity concentrations in bone ash samples were compared to the data of the respective soil samples. Figure 2 shows the enrichment of ^{90}Sr in bone ash samples compared to the soil samples (here we gave the values for the uppermost layer where in most cases the maximum concentrations were found as well as the fine roots of the feeding plants).

The enrichment or transfer factor (ratio activity concentration in bone ash to that in soil) found was between 2 and 3.8 with the exception of Saualpe / Mirniger Alm, where it was only 1.2. These values are only a rough estimation, as number of samples was low and animals of different age were investigated (see below). ^{210}Pb levels, on the other hand, were similar in animal bone ash and soil (transfer factor between 0.4 and 1.2). This reflects the fact that due to its chemical similarity with Ca ^{90}Sr is more easily transported to the bones than ^{210}Pb.

As the ^{90}Sr content in soil rises with altitude, the same is expected also for the ^{90}Sr content in deer bones. This correlation, however, is masked by the fact that bones from animals of different age were investigated. The bones of older animals contain higher amounts of ^{90}Sr per mass than bones of younger deer as ^{90}Sr is accumulated over the years. This can be seen from the deer hunted in relatively small and well defined areas as in Mariapfarr 1 (1350 m a.s.l.) and in Bächental (1250 m a.s.l.) (see Fig. 3 and 4). The same pattern has already been published for Neuwaldegg (Vienna) [6]. The animals hunted in the Kaprun area, however, did not show a clear activity concentration / age correlation. This might be due to the fact that the Kaprun area is too large: the valley is about 15 km long, leading from lowlands up to mountains. Here the influence of different feeding plants and the altitude factor seems to be predominant.

In Figure 5 the correlation of the ^{90}Sr activity concentration in bone ash with the site altitude is shown. A line of best fit is drawn through the dots representing 3 year old animals. Older animals (up to 9 years) mostly also fit this line which might imply a saturation effect for the uptake. Data of younger deer (up to 1 year), however, was found clearly below the line, revealing the fact that the amount of accumulated ^{90}Sr still was low.

Conclusions

The activity concentrations of anthropogenic (^{90}Sr, ^{137}Cs) and natural (^{238}U, ^{232}Th, ^{40}K, ^{210}Pb) radionuclides were determined in soil samples from different regions in Austria. The calculated activity concentrations of ^{40}K, ^{238}U and ^{232}Th were in the range of 230-709 $Bq.kg^{-1}$ for ^{40}K, 15-45 $Bq.kg^{-1}$ for ^{238}U and 30-46 $Bq.kg^{-1}$ for ^{232}Th, well within the world average range reported by UNSCEAR. The anthropogenic ^{137}Cs and ^{90}Sr contamination is due to global fallout in the fifties and early sixties of the last century and to the Chernobyl accident. Part of the investigated sites was struck by rainfall when the Chernobyl cloud passed by which led to lower $^{90}Sr/^{137}Cs$ ratios compared to sites where the global fallout was predominant. Generally, a direct proportional correlation

between the activity concentration of ^{90}Sr and ^{137}Cs in soil samples and site altitude was found.

Also the ^{90}Sr content in deer bones corresponds with the site altitude. This correlation can be seen more clearly if only animals of the same age are considered, as the ^{90}Sr content increases also with the age of the animal. Compared to older literature, our ^{90}Sr values in deer bones were lower, probably indicating a decreased bioavailability of ^{90}Sr bound to soil particles.

For the first time, the Sr Rad disk method for ^{90}Sr determinations was successfully applied to bone samples.

Acknowledgements

We thank all persons and institutions who provided deer bone samples.

References

1. Navas A, Soto J, Machin J (2002) Appl Radiat Isot 57:579
2. Singh S, Rani A, Mahajan R K (2005) Radiat Meas 39:431
3. Mehra R, Kumar S, Sonkawade R, Singh N P, Badhan K (2010) 59:1159
4. Karahan G, Bayulken A (2000) J Environ Radioact 47:213
5. Heinrich G, Gries A, Müller H, Oswald K (1989) Mitt Naturwiss Ver Steiermark 119:5
6. Landstetter C, Wallner G (2006) J Environ Radioact 87:315
7. Mietelski J W, LaRosa J, Ghods A (1993) J Radioanal Nucl Chem 170(1):243
8. Brun S, Bessac S, Uridat D, Boursier B (2002) J Radioanal Nucl Chem 253(2):191
9. Tatzber F, Irlweck K, Schaller F (1982) Wien Tierärztl Monatsschrift 69(3):86
10. Schönhofer F, Tataruch F, Friedrich M (1994) Sci Total Env 157:323
11. Pimpl M (1995) J Radioanal Nucl Chem 194(2):311
12. Jakopic R, Benedik L (2005) Acta Chim Slov 52:297
13. Grahek Z, Eskinja I, Kosutic K, Lulic S, Kvastek K (1999) J Radioanal Nucl Chem 241(3):617
14. Solecki J (2007) J Radioanal Nucl Chem 274(1):27
15. Galanda D, Rajec P, Matel L, Rosskopfova O, Dulanska S (2009) The Scientific World Journal 9:1206
16. Fiskum S K, Riley R G, Thompson C J (2000) J Radioanal Nucl Chem 245(2):261
17. Kameo Y, Katayama A, Fujiwara A, Haraga T, Nakashima M (20007) J Radioanal Nucl Chem 274(1):71
18. Beals D M, Britt W G, Bibler J P, Brooks D A (1998) J Radioanal Nucl Chem 236(1):187
19. Wallova G, Acharya K K, Wallner G (2010) J Radioanal Nucl Chem 283:713
20. Wallova G, Wallner G (2009) In: Eikenberg J, Jäggi M, Beer H, Baehrle H (eds) International conference on advances in liquid scintillation spectrometry, Davos, May 25-30, 2008. Radiocarbon, Tuscon, p 367
21. Wallova G, Kandler N, Wallner G (2010) J Radioanal Nucl Chem 286:429
22. Seymour R, Sergent F, Knight K, Kyker B (1992) Radioact Radiochem 3:14
23. Landstetter C, Ringer W, Achatz A, Katzlberger C (2010) J Radioanal Nucl Chem 286:435
24. Bem H, Bakir Y Y, Shuker S M (1991) J Radioanal Nucl Chem 147(2):263
25. Saxén R. (2002) In: Möbius S, Noakes J, Schönhofer F (eds) LSC 2001, Advances in liquid scintillation spectrometry. Radiocarbon, Tuscon, p 389
26. Svehla G (1979) Vogel´s textbook of macro and semimicro qualitative inorganic analysis, 5th edition, Longman, New York
27. United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) (2000) Sources and effects of ionizing radiation, vol I. United Nations, New York
28. Irlweck K, Khademi B (1996) J Radioanal Nucl Chem 203(1):79

29. United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) (1988) Sources, effects and risks of ionizing radiation, New York

30. United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) (1982) Ionizing radiation and sources and biological effects, New York

31. Mück K, Streit S, Steger F, Mayer K (1988) Bericht des Österreichisches Forschungszentrums Seibersdorf OEFZS – 4452, ST – 157/88

32. Srncik M, Hrnecek E, Steier P, Wallner A, Wallner G, Bossew P (2008) Radiochim Acta 96:733

33. Gastberger M, Steinhäusler F, Gerzabek M H, Lettner H, Humber A (2000) J Environ Radioact 49:217

Figures caption

Fig.1. ^{90}Sr activity concentrations in upper soil layer in dependence of site altitude.

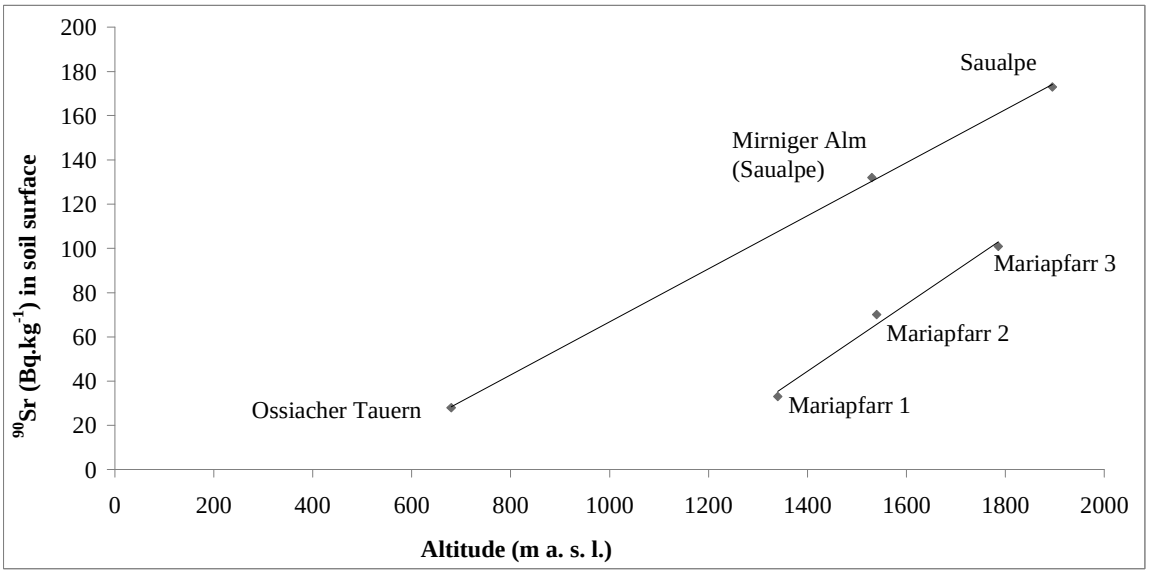


Fig. 2. Relationship between ^{90}Sr activity concentrations in bone ash samples and appropriate soil surface from Mariapfarr. Top 2 cm soil layer was used for calculations. The values for bone ash are average values from Tab. 3.

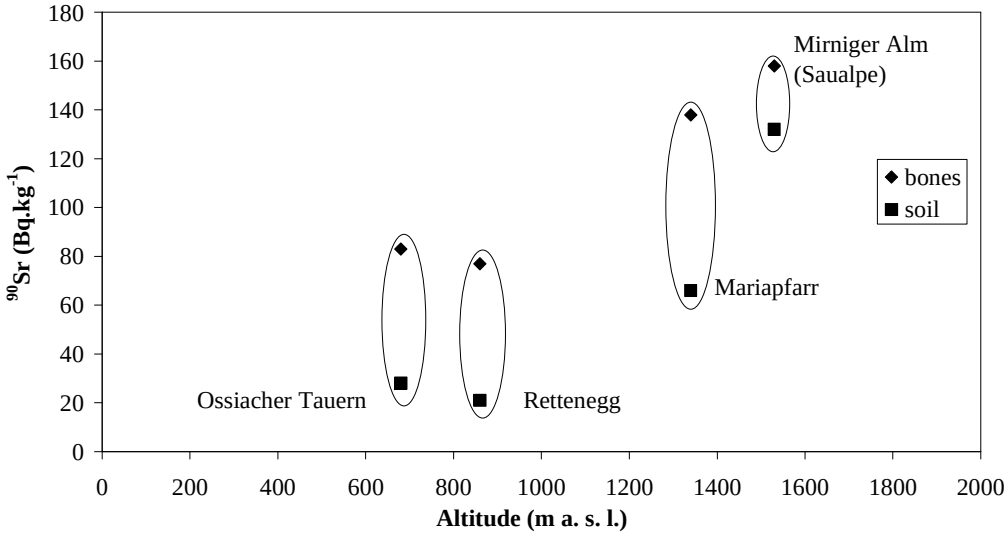


Fig.3. Age dependence on ^{90}Sr content in bone ash samples from Bächental region (1250 m a. s. l.).

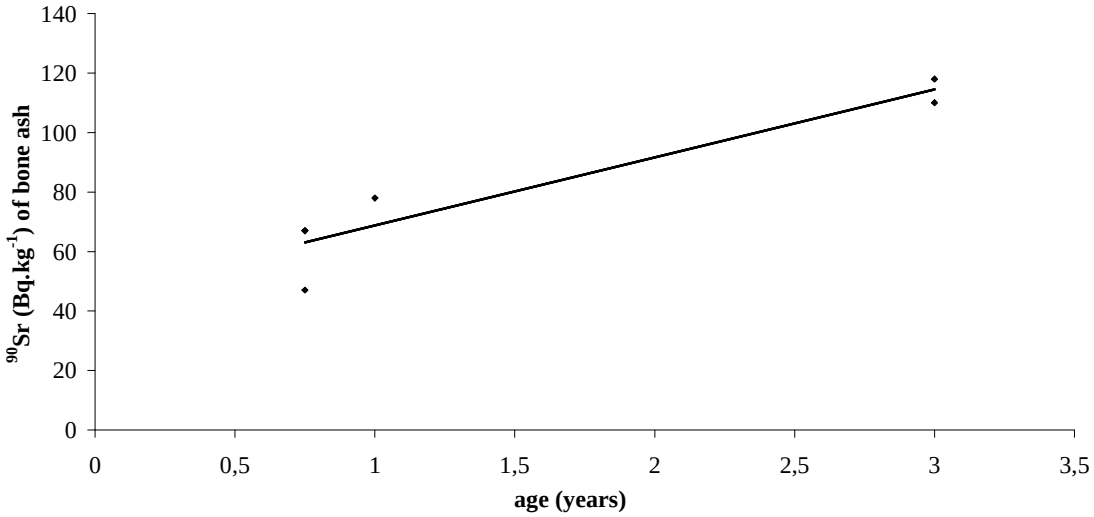


Fig. 4. Age dependence on ^{90}Sr content in bone ash samples from Mariapfarr region (1350 m. a. s. l.).

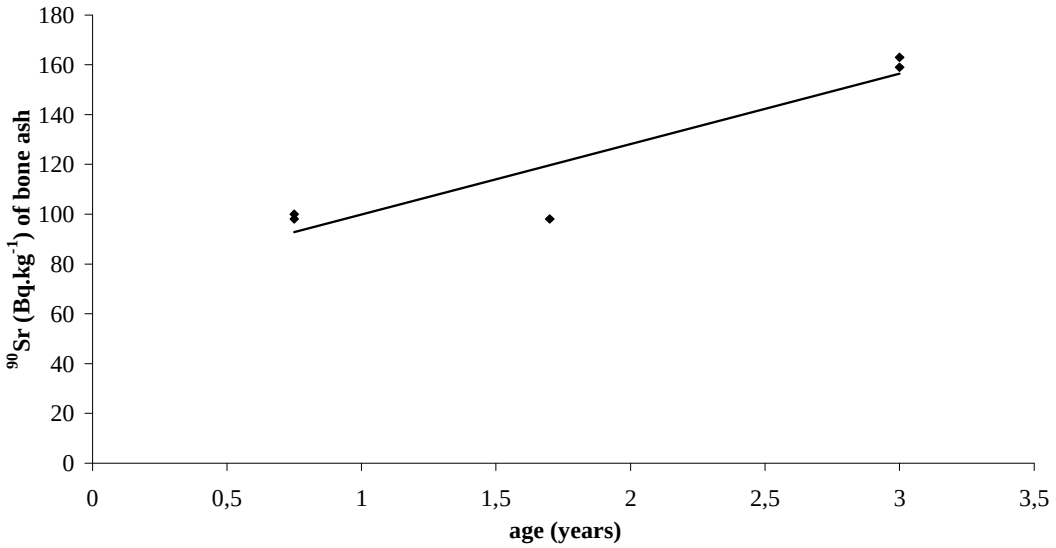
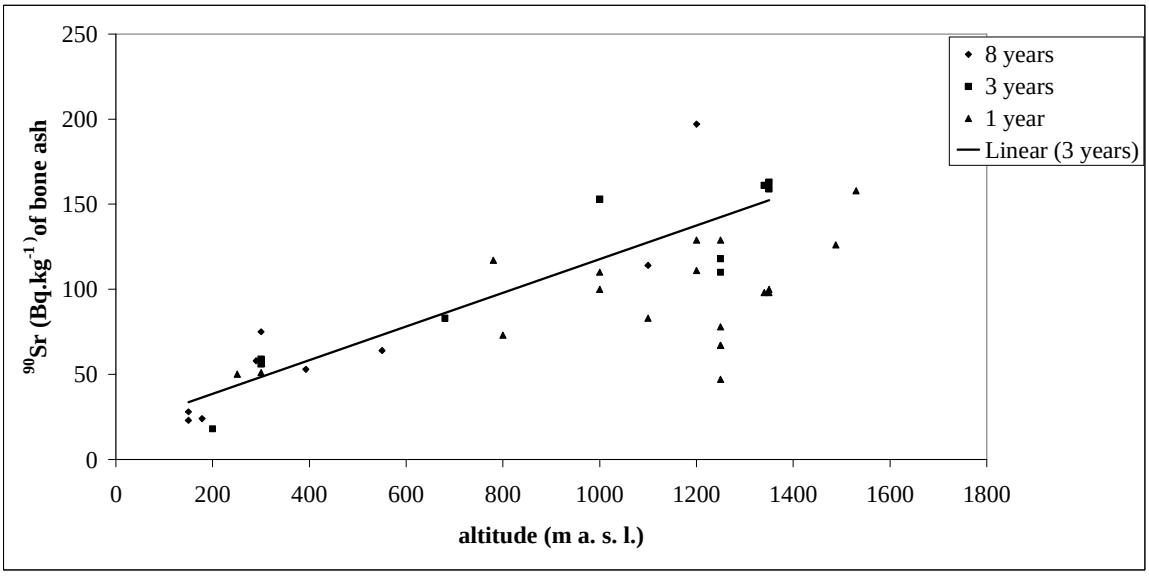


Fig. 5. Age and altitude dependence on ^{90}Sr content in bone ash samples from different regions of Austria.



Tables and diagrams

Table 1 Activity concentration of ^{210}Pb, ^{90}Sr and ^{137}Cs in soil samples together with $^{90}Sr/^{137}Cs$ isotopic ratios with 1σ uncertainties (reference date: 1st September 2005). Activity concentrations are calculated in $Bq.kg^{-1}$ of air dried soil samples.

site	soil depth (cm)	Altitude (m a.s.l)	^{210}Pb A ($Bq.kg^{-1}$)	^{90}Sr A ($Bq.kg^{-1}$)	^{137}Cs A ($Bq.kg^{-1}$)	$^{90}Sr/^{137}Cs$
Rettenegg	0-2 cm	860	32 ± 3	21 ± 3	315 ± 18	0.067 ± 0.01
	2-4 cm		39 ± 3	11 ± 3	304 ± 18	0.036 ± 0.01
	4-6 cm		34 ± 3	11 ± 3	127 ± 7	0.087 0.024
Kaltenegg	0-2 cm	1000	42 ± 4	8 ± 2	77 ± 3	0.104 ± 0.026
	2-4 cm		37 ± 3	8 ± 2	78 ± 3	0.103 ± 0.026
	4-6 cm		47 ± 5	8 ± 2	70 ± 2	0.114 ± 0.029
Ossiacher Tauern	0-2 cm	680	38 ± 3	28 ± 3	340 ± 18	0.082 ± 0.01
	2-4 cm		29 ± 3	19 ± 3	230 ± 17	0.083 ± 0.014
	4-6 cm		32 ± 4	12 ± 2	107 ± 6	0.112 ± 0.025
Saualpe	0-5 cm	1895	106 ± 7	173 ± 13	1800 ± 48	0.096 ± 0.008
Mirniger Alm (Saualpe)	0-2 cm	1530	41 ± 4	132 ± 10	1558 ± 44	0.085 ± 0.007
	2-4 cm		29 ± 3	164 ± 12	2051 ± 50	0.08 ± 0.006
	4-6 cm		14 ± 2	103 ± 7	1097 ± 30	0.094 ± 0.007
Mariapfarr 1	0-2 cm	1340	47 ± 5	33 ± 4	112 ± 10	0.295 ± 0.044
	2-4 cm		62 ± 5	33 ± 4	141 ± 7	0.234 ± 0.031
	4-6 cm		36 ± 3	24 ± 4	109 ± 6	0.22 ± 0.039
Mariapfarr 2	0-2 cm	1540	50 ± 5	70 ± 6	217 ± 13	0.323 ± 0.034
	2-4 cm		32 ± 3	64 ± 6	247 ± 17	0.259 ± 0.03
	4-6 cm		33 ± 3	66 ± 6	242 ± 17	0.273 ± 0.031
Mariapfarr 3	0-2 cm	1786	83 ± 6	101 ± 7	849 ± 27	0.119 ± 0.009
	2-4 cm		92 ± 6	53 ± 6	893 ± 30	0.059 ± 0.007
	4-6 cm		31 ± 3	22 ± 3	424 ± 14	0.052 ± 0.007

Table 2 Activity concentrations of ^{210}Pb and ^{90}Sr in bone samples (in $Bq.kg^{-1}$ of bone ash; in $Bq.kg^{-1}$ of fresh bone) from different areas of Austria with 1σ uncertainties (reference date: 1st September 2005).

site	age (years)	sex	Altitude (m a. s. l.)	^{210}Pb A ($Bq.kg^{-1}$) Ash	^{90}Sr A ($Bq.kg^{-1}$) ash	^{210}Pb A ($Bq.kg^{-1}$) bone	^{90}Sr A ($Bq.kg^{-1}$) bone
Nickelsdorf [a]	8-9	fem	150	7 ± 2	23 ± 3	3 ± 1	10 ± 3
Nickelsdorf	6-7	m	150	7 ± 2	28 ± 3	3 ± 1	13 ± 3
Petronell	5	m	175	10 ± 3	18 ± 3	5 ± 1	9 ± 2
Wolkersdorf	8	fem	178	7 ± 2	24 ± 3	2 ± 1	8 ± 2
Wien Sievering	3	fem	200	7 ± 2	18 ± 3	3 ± 1	9 ± 2
Hollabrun	2	fem	236	32 ± 4	22 ± 3	16 ± 3	11 ± 3
Neulengbach [a]	0.9	m	251	17 ± 3	50 ± 5	8 ± 2	24 ± 3
Hadersdorf	4-5	fem	270	8 ± 2	21 ± 3	4 ± 1	10 ± 3
Mannersdorf	6	fem	290	9 ± 2	58 ± 6	4 ± 1	23 ± 3
Neuwaldegg [a]	6	fem	300	10 ± 3	75 ± 6	5 ± 1	34 ± 3
Neuwaldegg	3	fem	300	16 ± 3	56 ± 6	8 ± 2	27 ± 3
Neuwaldegg	1	m	300	10 ± 3	51 ± 5	4 ± 1	19 ± 3
Neuwaldegg	3	fem	300	12 ± 3	59 ± 6	6 ± 2	28 ± 3
Ternitz	8	fem	393	26 ± 3	53 ± 6	12 ± 3	24 ± 3
St. Michael [a]	7-8	m	550	19 ± 3	64 ± 6	9 ± 2	29 ± 3
Melk [a]	?	?	550	18 ± 3	67 ± 6	8 ± 2	31 ± 3
Melk	?	?	550	16 ± 3	88 ± 6	7 ± 2	40 ± 4
Melk	?	?	550	9 ± 2	78 ± 6	4 ± 1	35 ± 3
Ossiacher Tauern	3	fem	680	20 ± 3	83 ± 6	9 ± 2	38 ± 4
Rettenegg	2	m	860	37 ± 3	77 ± 6	17 ± 3	35 ± 3
Treffning [a]	?	fem	1100	35 ± 3	74 ± 6	16 ± 3	34 ± 3
Liezen	0.75	fem	1100	19 ± 3	83 ± 6	9 ± 2	39 ± 4
Liezen	7-8	fem	1100	20 ± 3	114 ± 8	9 ± 2	53 ± 5
Mirnock [a]	6	fem	1200	35 ± 3	197 ± 13	16 ± 3	89 ± 6
Bächental	1	fem	1250	12 ± 3	78 ± 6	5 ± 1	35 ± 3
Bächental	3	fem	1250	14 ± 3	118 ± 8	6 ± 2	54 ± 5
Bächental	0.75	fem	1250	8 ± 2	67 ± 6	4 ± 1	31 ± 3
Bächental	3	fem	1250	20 ± 3	110 ± 8	9 ± 2	50 ± 5
Bächental	0.5	m	1250	10 ± 3	47 ± 5	4 ± 1	21 ± 3
Bächental	0,75	fem	1250	11 ± 3	67 ± 6	5 ± 1	30 ± 3
Mariapfarr	3	m	1350	54 ± 6	161 ± 12	25 ± 3	74 ± 6
Mariapfarr	0.75	m	1350	41 ± 4	98 ± 7	18 ± 3	44 ± 4
Mariapfarr [a]	?	?	1350	51 ± 5	248 ± 17	24 ± 3	114 ± 7
Mariapfarr	1.75	m	1350	51 ± 5	98 ± 7	23 ± 3	44 ± 4
Mariapfarr	0.75	m	1350	41 ± 4	100 ± 7	19 ± 3	46 ± 5
Mariapfarr	0.75	?	1350	41± 4	98 ± 7	18 ± 3	44 ± 4
Mariapfarr	3	?	1350	51 ± 5	163 ± 12	23 ± 3	74 ± 6
Mariapfarr	3	?	1350	51 ± 5	159 ± 11	23 ± 3	71 ± 6
Kaprun [a]	0.8	m	780	21 ± 3	117 ± 8	9 ± 2	53 ± 6
Kaprun 1	0.75	fem	800	14 ± 3	73 ± 6	6 ± 2	33 ± 3
Kaprun 2	1	m	1000	11 ± 3	110 ± 8	5 ± 1	50 ± 5
Kaprun 2	1	fem	1000	13 ± 3	100 ± 7	6 ± 2	45 ± 5
Kaprun 2	3	fem	1000	41 ± 4	153 ± 11	19 ± 3	70 ± 6
Kaprun 3	1	fem	1200	40 ± 4	129 ± 10	18 ± 3	59 ± 6

Kaprun 3	0.75	fem	1200	36 ± 3	111 ± 8	16 ± 3	51 ± 5
Kaprun 4	0.8	fem	1488	16 ± 3	126 ± 10	7 ± 2	55 ± 6
Kaprun 4		fem	1488	42 ± 4	142± 11	19 ± 3	65 ± 6
Mirniger Alm	1	m	1530	18 ± 3	158 ± 11	8 ± 2	71 ± 6
Gastein [b]	9	fem	1630	n.m.	n.m.	n.m.	268 ± 17
Kaunertal [b]	7	fem	1770	n.m.	n.m.	15 ± 3	375 ± 17

[a] - values adopted from previously published work [21]
[b] - values adopted from previously published work [6]
fem - female
m - male
? – unknown

Table 3 Activity concentrations of ^{90}Sr in bone ash determined by two steps method and by Sr Empore disk with 1σ errors (reference date: 1st September 2005). Activity concentrations are calculated in $Bq.kg^{-1}$ of bone ash.

sample	^{90}Sr two-step method A ($Bq.kg^{-1}$)	^{90}Sr Sr Empore disk A ($Bq.kg^{-1}$)
IAEA-A-12	29.8 ± 1.8	31.2 ± 2.5
Rettenegg/Kaltenegg	76.1 ± 5.2	78.5 ± 6.7
Ossiacher Tauern	81.7 ± 7.5	83.9 ± 11.1
Mirniger Alm	160.3 ± 12.1	157.6 ± 15.1
Mariapfarr 1, a	159.2 ± 10.1	162.9 ± 12.1
Mariapfarr 1, b	97.5 ± 7.7	98.5 ± 10.1

2.3.1 Supplementary investigations

In Chapter 2.3 (Monitoring of radionuclides in soil and bone samples) it was mentioned that specific activities of studied soils lie in the range of 30-46 Bq.kg^{-1} for ^{232}Th, 15-45 Bq.kg^{-1} for ^{238}U and 230-709 Bq.kg^{-1} for ^{40}K. These results are listed in Table 4. Aditionally, the soil sample from the middle part of Slovakia (Prievidza) was also investigated and added to the Table 4.

Table 4. The activity concentrations of ^{228}Ac, ^{212}Pb and ^{208}Tl (^{232}Th daughter products) and ^{214}Pb, ^{214}Bi and ^{226}Ra (^{238}U daughter products) in investigated soil samples with corresponding 1σ errors.

site	Soil depth (cm)	altitude (m.a.s.l.)	^{232}Th series (Bq.kg^{-1})			^{238}U series (Bq.kg^{-1})		
			^{228}Ac	^{212}Pb	^{208}Tl	^{214}Pb	^{214}Bi	^{226}Ra
Prievidza	0-2 cm	600	24 ± 2	25 ± 2	21 ± 2	14 ± 1	16 ± 1	16 ± 1
Prievidza	2-4 cm		34 ± 3	36 ± 3	36 ± 3	16 ± 1	20 ± 2	17 ± 1
Prievidza	4-6 cm		29 ± 2	29 ± 2	32 ± 3	17 ± 1	18 ± 1	20 ± 2
Rettenegg	0-2 cm	860	46 ± 4	47 ± 4	45 ± 4	27 ± 2	30 ± 3	30 ±3
Rettenegg	2-4 cm		38 ± 3	37 ± 3	41 ± 3	27 ± 2	31 ± 3	26 ± 2
Rettenegg	4-6 cm		42 ± 3	45 ± 4	42 ± 3	34 ± 3	37 ± 3	32 ± 3
Kaltenegg	0-2 cm	1000	46 ± 4	44 ± 4	46 ± 4	28 ± 2	29 ± 2	26 ± 2
Kaltenegg	2-4 cm		48 ± 4	45 ± 4	46 ± 4	30 ± 3	32 ± 3	30 ± 3
Kaltenegg	4-6 cm		43 ± 3	40 ± 3	46 ± 4	28 ± 2	32 ± 3	28 ± 2
Ossiacher Tauern	0-2 cm	680	44 ± 4	48 ± 5	45 ± 4	37 ± 3	35 ± 3	38 ± 3
Ossiacher Tauern	2-4 cm		40 ± 4	48 ± 5	45 ± 4	30 ± 3	32 ± 3	32 ± 3
Ossiacher Tauern	4-6 cm		37 ± 3	39 ± 4	36 ± 3	29 ± 2	33 ± 3	32 ± 3
Saualpe	0-5 cm	1895	35 ± 3	36 ± 3	36 ± 3	22 ± 2	23 ± 2	22 ± 2
Mierniger Alm	0-2 cm	1530	44 ± 4	46 ± 4	45 ± 4	31 ± 3	31 ± 3	30 ± 3
	2-4 cm		39 ± 4	41 ± 3	43 ± 4	25 ± 2	28 ± 2	28 ±2
	4-6 cm		43 ± 4	46 ± 4	47 ± 4	36 ± 3	39 ± 4	36 ± 3
Mariapfarr 1	0-2 cm	1340	36 ± 3	39 ± 4	37 ± 3	26 ± 2	23 ± 2	23 ± 2
	2-4 cm		35 ± 3	33 ± 3	34 ± 3	28 ± 2	33 ± 3	27 ± 2
	4-6 cm		31 ± 3	36 ± 3	31 ± 3	28 ± 2	27 ± 2	24 ± 2
Mariapfarr 2	0-2 cm	1540	38 ± 3	39 ± 4	34 ± 3	32 ± 3	30 ± 3	33 ± 3
	2-4 cm		33 ± 3	28 ± 2	28 ± 2	33 ± 3	28 ± 2	33 ± 3
	4-6 cm		41 ± 3	37 ± 3	44 ± 4	30 ± 3	35 ± 3	31 ± 3
Mariapfarr 3	0-2 cm	1786	37 ± 3	35 ± 3	38 ± 3	45 ± 4	45 ± 4	45 ± 4
	2-4 cm		34 ± 3	37 ± 3	37 ± 3	34 ± 3	33 ± 3	32 ± 3
	4-6 cm		33 ± 3	36 ± 3	34 ± 3	34 ± 3	31 ± 3	30 ± 3

From obtained specific activities of ^{40}K, ^{238}U and ^{232}Th the absorbed dose rates in air ($nGy.h^{-1}$) 1m above ground and annual effective dose rates outdoors ($mSv.y^{-1}$) were calculated. The absorbed dose rates in air 1m above ground varies between 46 – 73 $nGy.h^{-1}$ (the population-weighed value published by UNSCEAR is 60 $nGy.h^{-1}$). The UNSCEAR report also published the range for absorbed dose rate in air in Austria (1980) to 20-150 $nGy.h^{-1}$(average value 43 $nGy.h^{-1}$). The average value estimated in this work is 59 $nGy.h^{-1}$. According the UNSCEAR report, an outdoor occupancy factor of 0.2 and a conversion coefficient of 0.7 $Sv.Gy^{-1}$ were used. The annual effective dose (outdoors) was found to be between 0.05 - 0.08 $mSv.y^{-1}$ with an average value of 0.07 $mSv.y^{-1}$ (world-wide average: 0.07 $mSv.y^{-1}$). The detailed results together with data obtained for soil from Prievidza are given in Table 5 and Table 6.

Table 5. The activity concentrations of ^{238}U, ^{232}Th and ^{40}K ($Bq.kg^{-1}$) in investigated soil samples with corresponding 1σ errors.

site	soil depth (cm)	^{232}Th $Bq.kg^{-1}$	^{232}Th (mean) $Bq.kg^{-1}$	^{238}U $Bq.kg^{-1}$	^{238}U (mean) $Bq.kg^{-1}$	^{40}K $Bq.kg^{-1}$	^{40}K (mean) $Bq.kg^{-1}$
Prievidza	0-2 cm	23 ± 2	29 ± 3	15 ± 1	17 ± 1	571 ± 16	344 ± 18
	2-4 cm	35 ± 3		18 ± 1		230 ± 10	
	4-6 cm	30 ± 3		18 ± 1		231 ± 10	
Rettenegg	0-2 cm	46 ± 4	43 ± 4	29 ± 2	30 ± 3	504 ± 19	513 ± 19
	2-4 cm	39 ± 4		28 ± 2		500 ± 18	
	4-6 cm	43 ± 4		34 ± 3		534 ± 19	
Kaltenegg	0-2 cm	45 ± 4	45 ± 4	28 ± 2	29 ± 2	494 ± 17	500 ± 18
	2-4 cm	46 ± 4		31 ± 3		495 ± 17	
	4-6 cm	43 ± 4		29 ± 2		510 ± 19	
Ossiacher Tauern	0-2 cm	46 ± 4	42 ± 4	37 ± 3	33 ± 3	347 ± 18	344 ± 17
	2-4 cm	44 ± 4		31 ± 3		382 ± 18	
	4-6 cm	37 ± 3		31 ± 3		302 ± 16	
Saualpe	0-5 cm	36 ± 3	36 ± 3	22 ± 2	22 ± 2	263 ± 15	263 ± 15
MiIrniger Alm	0-2 cm	45 ± 4	44 ± 4	31 ± 3	32 ± 3	239 ± 17	281 ± 16
	2-4 cm	41 ± 3		27 ± 2		274 ± 16	
	4-6 cm	45 ± 4		37 ± 3		329 ± 16	
Mariapfarr 1	0-2 cm	37 ± 3	35 ± 3	24 ± 2	26 ± 2	628 ± 20	650 ± 20
	2-4 cm	34 ± 3		29 ± 2		709 ± 21	
	4-6 cm	33 ± 3		26 ± 2		612 ± 18	
Mariapfarr 2	0-2 cm	37 ± 3	36 ± 3	32 ± 3	32 ± 3	434 ± 17	467 ± 17
	2-4 cm	30 ± 3		31 ± 3		523 ± 19	
	4-6 cm	41 ± 3		32 ± 3		445 ± 17	
Mariapfarr 3	0-2 cm	37± 3	36 ± 3	45 ± 4	37 ± 3	671 ± 21	517 ± 18
	2-4 cm	36 ± 3		33 ± 3		448 ± 17	
	4-6 cm	34 ± 3		32 ± 3		428 ± 17	

Table 6. Calculated absorbed dose rates in air 1m above ground ($nGy.h^{-1}$) and the annual effective dose rates outdoors ($mSv.y^{-1}$).

site	soil depth (cm)	Absorbed dose rate ($nGy.h^{-1}$) 1m above ground	Absorbed dose rate ($nGy.h^{-1}$) 1m above ground (mean)	Annual effective dose ($mSv.y^{-1}$) outdoors	Annual effective dose ($mSv.y^{-1}$) outdoors (mean)
Prievidza	0-2 cm	47	42	0.057	0.051
	2-4 cm	41		0.051	
	4-6 cm	38		0.046	
Rettenegg	0-2 cm	65	63	0.079	0.078
	2-4 cm	59		0.073	
	4-6 cm	66		0.081	
Kaltenegg	0-2 cm	63	64	0.077	0.078
	2-4 cm	65		0.08	
	4-6 cm	63		0.077	
Ossiacher Tauern	0-2 cm	61	57	0.074	0.07
	2-4 cm	59		0.072	
	4-6 cm	51		0.063	
Saualpe	0-5 cm	46	46	0.056	0.056
Mierniger Alm	0-2 cm	53	55	0.065	0.067
	2-4 cm	51		0.062	
	4-6 cm	60		0.074	
Mariapfarr 1	0-2 cm	62	62	0.076	0.076
	2-4 cm	65		0.079	
	4-6 cm	60		0.072	
Mariapfarr 2	0-2 cm	57	58	0.069	0.071
	2-4 cm	56		0.069	
	4-6 cm	60		0.074	
Mariapfarr 3	0-2 cm	73	62	0.089	0.075
	2-4 cm	57		0.07	
	4-6 cm	55		0.067	

The activity concentrations of ^{137}Cs, ^{90}Sr and ^{210}Pb in soil sample from Slovakia (Table 7) were determinated according the procedures described in section 2.3.

Table 7. Activity concentration of ^{210}Pb, ^{90}Sr and ^{137}Cs in soil samples together with $^{90}Sr/^{137}Cs$ isotopic ratios with 1σ uncertainties (reference date: 1 st September 2005). Activity concentrations are calculated in $Bq.kg^{-1}$ of air dried soil samples.

site	soil depth (cm)	altitude (m. a. s. l)	^{210}Pb A ($Bq.kg^{-1}$)	^{90}Sr A ($Bq.kg^{-1}$)	^{137}Cs A ($Bq.kg^{-1}$)	$^{90}Sr/^{137}Cs$
Prievidza	0-2 cm	600	18 ± 2	3 ± 1	9 ± 4	0.333 ± 0.19
	2-4 cm		21 ± 2	1 ± 1	4 ± 2	0.250 ± 0.28
	4-6 cm		18 ± 2	2 ± 1	6 ±2	0.333 ± 0.19

The activity concentrations of ^{90}Sr and ^{210}Pb were determinated in two bone samples from Prievidza (Table 8). For this purpose the two-step procedure and Empore disks were used (experimental part described in section 2.3).

Table 8. Activity concentrations of ^{90}Sr in bone sample from Slovakia determined by two steps method and by Sr Empore disk together with activity concentration of ^{210}Pb with 1σ errors (reference date: 1st September 2005). Activity concentrations are calculated in $Bq.kg^{-1}$ of bone ash.

site	hunted	sex	age	^{90}Sr/two-steps method A ($Bq.kg^{-1}$)	^{90}Sr/Empore disk A ($Bq.kg^{-1}$)	^{210}Pb/two-steps method A ($Bq.kg^{-1}$)
Prievidza	6.2.2008	male	4 Y	28.3 ± 3.1	29.4 ± 4.8	14.5 ± 5.3
Prievidza	6.2.2008	female	3 Y	19.4 ± 3.2	17.7 ± 2.7	18.7 ± 4.7

The teeth of my son Peter Walla were studied for ^{90}Sr content. The short Sr Spec method (section 2.3) was used. Peter Walla was born on 4th April 2003 in Handlova (Slovakia) and since 2005 he has lived in Vienna (Austria). The teeth were collected from September to November 2009. The activity concentration of ^{90}Sr was found to be 27.9 ± 2.9 $Bq.kg^{-1}$ (reference date: 1st September 2005).

2.4 Fast determination of Po-210 in urine by LSC as a means to estimate deliberate poisioning

Wallner G, Schönhofer F, Wallova G, Steger F (Okt. 2010) accepted for publication in LSC 2010, Advances in Liquin Scintillation Spectrometry, 6-10 September 2010, Paris, France, Radiocarbon, Tuscon

FAST DETERMINATION OF Po-210 IN URINE BY LSC AS A MEANS TO ESTIMATE DELIBERATE POISIONING

Gabriele Wallner (1), Franz Schönhofer (2), Gabriela Wallova (1), Ferdinand Steger (3)

(1) Institut für Anorganische Chemie, Universität Wien, Währinger Str. 42, A-1090 Vienna, Austria
(2) BMLFUW – Radiation Protection Department – retired, present address: Habicherg. 31/7, A-1160 Vienna, Austria
(3) NES – Nuclear Engineering Seibersdorf – retired, present address: Anton Baumgartnerstraße 44/A4/223, A-1230 Vienna, Austria

Abstract

Calculations show that in case of allegedly poisoning a Po-210 body burden leading to the death of the victim (about 1-3 GBq) should be easily detectable from the urine excretion because the activity concentration is probably between 0.07 and 0.7 Bq/mL. Such activity levels can be detected easily via LSC without any chemical separation within a very short time – less than a few hours. Due to its similar α-energy Pu-239 would interfere with the Po-210 measurement. We investigated the possibility of determining the Po-210 body burden by measuring it in simulated urine samples by liquid scintillation counting. For separation of Po from other radionuclides (especially Pu) we present three very quick methods using the Po extractive LSC cocktail POLEX®, the resin Sr·Spec® and the Sr Rad Disk®: all three extract Po with an efficiency of more than 90%, while Pu is not extracted into POLEX® and retained neither on the Sr·Spec® column nor on the Sr Rad Disk®.

Introduction

Po-210, a decay product of U-238, was discovered in Paris by Marie and Pierre Curie in the year 1898 and was named in honour of Marie´s home country Poland. With a half life of 138 days, it decays by α-emission to the stable lead isotope Pb-206.

Although it is extremely rare in nature (its concentration is only about 0.1mg/t of uranium ore) Po-210 can be found in higher concentrations in drinking water from wells or in mineral water (a few mBq/L up to ~100 mBq/L (Isam Salih et al. 2002). Originally radon and its daughter products were explicitly excluded in the EC Drinking Water Directive (1998), but then for Po-210 in drinking water a reference maximum concentration of 0.1 Bq/L was given in the EC Recommendation K (2001). Likewise it is present in seawater and it is well known that especially shellfish accumulate Po-210. So the main portion of dose to the populations living near Mururoa and Fangataufa in the South Pacific is due to natural Po-210 incorporated via the traditional food and not, as one might suspect, due to former French nuclear tests (IAEA 1999). The same is true for people living in Cumbria (UK) near the Sellafield nuclear installation (McDonald et al. 1986) or near the La Hague (F) reprocessing plant (Beutier et al. 2000). E. Holm (1994) reported that the dose to the population from Po-210 originating from the consumption of fish from the Baltic Sea is similar to that of Cs-137, even after the Chernobyl accident. For Canadians of aboriginal origin Po-210 is contributing 57 to 72% of the total accumulated intake. This is due almost entirely to the ingestion pathway and to one particular food chain (lichen – reindeer – humans) (Tracy 1993).

Besides water and food, also other consumer products widely used contain Po-210, sometimes in not negligible concentrations and quantities. Po-210 is used in static eliminators, dust removers and spark plugs as well as in portable Po(Be) neutron sources (in former times it was also used in short lived isotope batteries and as atomic bomb triggers). Last but not least the

abundance of Po-210 in tobacco and subsequently in cigarette smoke should not be forgotten. Dalheimer et al. (2007) recently reported a daily urinary excretion median value of 3.5 mBq/d for non-smokers and 6.6 mBq/d for smokers.

Artificially, Po-210 is produced by neutron activation of bismuth (Bi-209 is quasi-stable with a half-life of 1.9·1019 a). The activation product Bi-210 is a β-emitter with a half-life of 5 days and decays to Po-210. The worldwide production is estimated to about 100 g per year.

Po-210 is extremely radiotoxic if incorporated (inhaled or ingested). The ICRP model (ICRP, 1993) and also a more recent model by Leggett and Eckerman (2001) assume that about 10% of the intake is absorbed into blood. According to the current model for the systemic behaviour after uptake to blood given in the above cited publications it is widely distributed in soft tissues but with higher than average concentrations in kidneys, liver, spleen and bone marrow. Its biological half-life is supposed to be about 50 days in all organs. Combined with the physical half-life of 138 days this leads to an effective retention half-time in the body of 37 days with one third of the excretion going to urine (in the first few days after intake the predominant excretion route is faeces). As in vivo measurements with external gamma ray detectors are not possible due to the very low photon emission probability of Po-210, the only practicable proof of incorporation is via measurement of excretion samples. Although there is more activity present in a daily sample of faeces, urine measurements are preferred since chemical procedures for Po extraction are much easier with urine samples.

According to a literature search there seems to be one case known, when a Japanese researcher at Marie Curie´s lab was poisoned due to his work with Po-210 and a second case in Russia, when a worker accidently inhaled an aerosol of Po-210 (Perkins 2007). Both persons died as a consequence. In November 2006 mass media informed about the allegedly poisoning of Mr. Alexander Litvinenko in London with at that time still unknown poisioning agent. The first idea of a thallium poisoning had to be abandoned soon

because with modern analytical equipment it is extremely easy to confirm any incorporated thallium within very short time. Secondly radioactive thallium was suspected. Thallium-201 is widely used in nuclear medicine, but since it is a gamma-emitter the amount needed to kill a person would be incredibly high. Anyway, urine samples did not show any gamma-contaminations. The third guess was that he might have been poisoned with Po-210. In a retrospective view it is surprising that urine samples were not checked for alpha-emitters because it would have been an easy task with the equipment usually available in hospitals (as e.g. liquid scintillation counters).

In this paper we present a very quick method to determine clearly elevated Po-210 levels in urine samples by liquid scintillation counting (LSC). This means that only very little or no handling of the sample is necessary, and that the result is available within a few hours latest. For the definite identification of the alpha-emitter as Po-210 we describe 3 short extraction methods.

Methods and results

In Li et al. (2008) an absorbed dose of 5 Gy to red marrow, 6 Gy to kidneys and 8 Gy to liver were applied as organ lethal doses to estimate the possible Po-210 intake of Mr. Litvinenko. By using the ICRP model and the model by Leggett and Eckerman (2001) they calculated administered amounts of 27 to 1,408 MBq, corresponding to 0.2 to 8.5 µg of Po-210. This is consistent with the estimates of Harrison et al. (2007), who concluded that 0.1-0.3 GBq or more absorbed to blood would be fatal for an adult male. Assuming 10% absorption to blood, this corresponds to an ingestion of 1-3 GBq. The daily urinary excretions after acute ingestion of 1 Bq of Po-210 calculated following the ICRP (1993) model and that of Leggett and Eckman (2001) are between 1·10-4 and 1·10-3 Bq/d (Li et al. 2008), giving 105-106 Bq of Po-210 in the daily urine after ingestion of 1 GBq. The excretion rate stays rather constant after two days until about 100 days after intake. This prevents the determination of the date of the poisoning, but enables the estimation of the administered amount of Po-210 over a longer time period. Assuming a daily

urine excretion of 1500 mL gives us a Po-210 activity concentration in urine of 67 to 670 Bq/mL. Even an intake of 1 MBq Po-210 (non lethal and not acutely detrimental) causing a urine concentration of 0.067 to 0.67 Bq/mL (or 4 to 40 dpm/mL) is easily accessible to modern counting techniques.

Direct measurement of α-emitters in urine

A very quick estimate of the order of magnitude of activity concentration of any α-emitter in urine in the case of poisoning is possible by a direct LSC measurement. Using a Quantulus®1220 low-level counter (Wallac Oy, Finland, now Perkin Elmer) with pulse-shape analysis enables to differentiate quantitatively between α- and β-emitters. The counting efficiency for alphas is very close to 100% and almost independent of the quench level. The background in the respective region is 0.4 cpm, corresponding to 0.007 Bq per sample. After dilution of 1-3 mL of urine 1:1 with distilled water (to reduce the colouring) and mixing with 18-14 mL of the scintillation cocktail HiSafe®III (Perkin Elmer) the sample is measured. A reasonably accurate result is available after a counting time of 10 to 100 min.

While other α-emitters can be ruled out by the shape of their spectrum (double peaks for uranium and thorium) or by their energies (besides their use as a poison being very unlikely), the only thinkable interference for a possible (criminal or terroristic) radionuclide attack is Pu-239. Its decay energy of 5.16 MeV is very close to that of Po-210 (5.30 MeV) and hence these two nuclides cannot be distinguished by LSC. Therefore a separation procedure is necessary to distinguish the alpha emissions between polonium and plutonium.

The most common technique for Po-210 determination in environmental samples is auto-deposition on a Cu or Ag planchette followed by α-spectrometry (WHO 1966). However, processing the sample needs a few hours and this seems to be too long in a case of emergency. Another well known method is the extraction of Po into the extractive cocktail POLEX® (to separate it from Pb-210 and eventually also from Bi-210) and measurement

by LSC (McDowell and McDowell 1991, Wallner 1997, Wallner and Irlweck 1997, Katzlberger et al. 2001, Wallner et al. 2002). Especially for small samples the chemical procedure can be done in about 10 min. Also available in many labs are Sr·Spec® resin (Triskem company) and Sr Rad disks® (3M Empore), a solid phase extraction resin and a membrane loaded with a crown ether. It is well known that Sr·Spec®resin (originally developed for strontium separation by Horwitz et al. 1991, 1992) can also be used for Pb-210 and Po-210 extraction (Vajda et al. 1997, Vrecek et al. 2004, Kim et al. 2009). We investigated also the Sr Rad disks® in this respect and found it suitable for Po separation as well. After elution of the polonium from the resin or the membrane the subsequent Po-210 measurement is again done by LSC.

Po-210 extraction by POLEX®

All separation experiments were done in three steps: first the procedure for a complete separation of Po from the urine matrix was developed (step 1) and then the behaviour of plutonium under these conditions was investigated (step 2). A “mixed” sample was prepared for the final test (step 3): a urine sample (usually 1 mL) was spiked with 0.6 Bq Po-210 and 0.8 Bq Pu-239. We give here the procedure for the double-spiked sample.

The sample (usually 1 mL) was diluted 1:1 with distilled water, and then the resulting volume was doubled by adding conc. phosphoric acid. This mixture was shaken with 2 mL of POLEX® and after 10 min waiting for phase separation an aliquot of the POLEX® phase was measured by LSC.

The extraction efficiency for polonium was at least 95%. The blank value was 0.02 cpm (corresponding to 0.3 mBq per sample), lower than with the direct method (because the cocktail volume is much smaller and a pure organic phase is measured), provided the used phosphoric acid had been carefully selected with respect to its Pb-210 content (Wallner 1998). Pu is not extracted from the aqueous phase under these conditions and can also be measured by LSC after mixing of the aqueous phase with HiSafe®III.

Po-210 extraction with Sr·Spec®resin

We used the procedure of Vajda et al. (1997) for Po-210 separation from the urine matrix (step1). A second urine sample was spiked with Pu-239 and the rinsing solution was checked for plutonium recovery (step 2). The whole procedure is again given for the double-spiked sample (step 3).

For conditioning, 3 g of the resin were soaked in distilled water for 1 hour, transferred to the column and rinsed with 50 mL of distilled water and 50 mL of 2M HCl (both saturated with n-octanol). The diluted urine was adjusted to 2M HCl and loaded onto the column. The column was rinsed with 3 mL of 2M HCl, and in this first fraction 100% of the plutonium was found, as it is not retained on the resin. Subsequently Po-210 was rinsed in 3 fractions of 3 mL, 5 mL and again 5 mL of 6M HNO3. Each fraction was mixed with HiSafe®III and measured by LSC: 42%, 53% and 5-6% of Po-210 were recovered. This means that at least 8 mL of eluant are necessary to achieve about 95% Po-210 recovery. This amount of acid was evaporated to dry and the residue was then taken up into 2 mL of 2 M HNO_3 and mixed with the LSC cocktail.

With the resin already conditioned, the processing time is about half an hour. The achievable background is the same as with the direct measurement (0.4 cpm).

Po-210 extraction with Sr Rad Disk®

The Sr Rad disk (3M Empore) is a membrane loaded with a crown ether (similar to Sr·Spec®resin) and is used like a filter to extract Sr (Seely et al. 1998, Smith et al. 1996). As the chemistry involved seems to be similar to that of Sr·Spec®resin, we also investigated the membrane for Po-210 extraction.

The urine (1 mL) was diluted 1:1 with water, adjusted to 2M HCl, and 0.6 Bq Po-210 were added (step 1). After rinsing the Sr Rad disk with methanol and 2M HCl the sample was slightly sucked through the membrane. With a sample acidity of 2M HCl, however, Po was only partially retained on the filter, but enhancing the acidity to 6M HCl resulted in 100% Po extraction yield. Then an equivalent sample with 0.8 Bq Pu-239 added was investigated (step 2). In the filtrate about 50% of the plutonium was found, additional rinsing with 4 mL of 6M HCl removed plutonium completely from the disk. A double-spiked sample (step 3) was processed as follows: after washing plutonium completely from the disk, Po-210 was eluted with 4 mL of basic 0.05M EDTA solution. The EDTA solution is mixed with HiSafe®III and measured by LSC.

Here the processing time is again only about 10-15 min. The achievable background is the same as with the direct measurement (0.4 cpm).

Conclusions

Clearly, elevated Po-210 levels in urine samples after acute intake of about 1 MBq Po-210 can be detected still after 120 days by liquid scintillation counting (LSC). In the case of deliberate poisoning the administered activity is expected in the order of 1 GBq, therefore the measurement of the excreted activity would be trivial. In a first test the urine sample can be measured by LSC directly without any pre-treatment. For the definite identification of the alpha-emitter as Po-210 (discrimination against Pu-239) we developed 3 short separation methods using the extractive cocktail Polex®, the Sr·Spec®resin and the Sr Rad disk®, respectively. Only very little handling of the sample is necessary, and the results are available within a few hours latest. Therefore these fast methods are well suited in emergency situations when measurements of incorporated activities are a prerequisite for further decisions.

References

Beutier D., Dellero N., Pradel J. (2000) Comparing the dose contributions from man made and from natural radioactivity. Proc. Int. Conf. IRPA-10, Hiroshima, May 14-19, P-4b-239

Commission Recommendation of 20 December 2001 on the protection of the public against exposure to radon in drinking water supplies (2001/928/Euratom)

Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption, Official Journal L 330, 05/12/1998 p. 0032-0054

Dalheimer A., König K., Noßke D., Schäfer I. (2007) Der Hamburger Poloniumfall aus Sicht der Inkorporationsüberwachung. In: Bayer A., Faleschini H., Krüger S., Strobl Chr. (Herausgeber) Vorkehrungen und Mssnahmen bei Radiologischen Ereignissen. 5. Seminar des Arbeitskreises Notfallschutz. Augsburg, 25.-27-4-2007. Bericht Nr. FS-07-142-AKN. Publikationsreihe Fortschritte im Strahlenschutz. Fachverband für Strahlenschutz e.V., TÜV Media GmbH, Köln, pp. 82-88.

Harrison J., Leggett R., Lloyd D., Phipps A., Scott B. (2007) Polonium-210 as a poison. J. Radiol. Prot. 27: 17-40

Holm E. (1994) Polonium-210 and radiocesium in muscle tissue of fish from different Nordic marine areas. In: H. Dahlgaard, ed., Nordic Radioecology – The transfer of radionuclides through Nordic ecosystems to man. Studies in Environmental Science 62, Elsevier, The Netherlands.

Horwitz, E.P., Dietz, M.L., Fischer, D.E. (1991) Separation and Preconcentration of Sr from Biological, Environmental, and Nuclear Waste Samples by Extraction Chromatography Using a Crown Ether, Anal. Chem. 63, 522-525.

Horwitz, E.P., Chiarizia, R., Dietz, M.L. (1992) A novel strontium-selective extraction chromatographic resin. Solvent Extraction and Ion Exchange 10 (2), 313-336.

International Atomic Energy Agency (IAEA) (1999) Radiological Situation at the Atolls of Mururoa and Fangataufa: Summary Report. Radiological Assessment Reports Series, ISBN 92-0-101298-5

ICRP Publ. No. 67, Part 2, Annals of the ICRP 23(3/4), (1993)

Isam Salih, M.M., Pettersoson, H.B.L., Lund, E. (2002) Uranium and thorium series radionuclides in drinking water from drilled bedrock wells: correlation to geology and bedrock radioactivity and dose estimation. Rad. Prot. Dosim. 102(3), 249-258.

Katzlberger, C., Wallner, G., Irlweck, K. (2001) Determination of 210Pb, 210Bi and 210Po in natural drinking water. J. Radioanal. Nucl. Chem. 249/1, 191-196.

Kim C.-K., Lee M.H., Martin P. (2009) Method validation of a procedure for determination of 210Po in water using DDTC solvent extraction and Sr resin. J. Radioanal. Nucl. Chem. 279(2), 639-646.

Leggett R.W., Eckerman K.F. (2001) A systemic biokinetic model for polonium. Sci. Total Environ. 275: 109-125

Li W.B., Gerstmann U., Giussani A., Oeh U., Paretzke H.G. (2008) Internal dose assessment of 210Po using biokinetic modeling and urinary excretion measurement. Radiat. Environ. Biophys. 47: 101-110

McDonald P., Fowler S.W., Heyraud M., Baxter M.S. (1986) Polonium-210 in mussels and its implications for environmental alpha-autoradiography. JENVRAD 3(4), 293-303.

McDowell W.J., McDowell B.L. (1991) Liquid Scintillation Alpha-Spectrometry: a Method for Today and Tomorrow. Proc. Int. Conf. on New Trends in Liquid Scintillation Counting and Organic Scintillators 1989. Eds.: H. Ross, J.E. Noakes and J.D. Spaulding. Lewis Publ. Inc., Michigan 1991.

Perkins A.C. (2007) The London Polonium Poisoning: Events and Medical Implications. World Journal of Nuclear Medicine 6(2), 102-106.

Seely D.C., Osterheim J.A. (1998) Radiochemical analyses using Empore® Disk technology. J. Radioanal. Nucl. Chem. 236(1-2), 175-180

Smith L.L., Orlandini K.A., Alvarado J.S., Hoffmann K.M., Seely D.C., Shannon R.T. (1996) Application of Empore® Strontium Rad Disks to the Analysisof Radiostrontium in Environmental Water Samples. Radiochimica Acta 73, 165-170

Tracy B.L. (1993) Exposure of northern Canadians to natural and artificial radioactivity in caribou meat. In: P. Strand and E. Holm, eds., Environmental Radioactivity in the Arctic and Antarctic, Norwegian Radiation Protection Authority, Osteras, Norway, pp. 371-374.

Vajda N., LaRosa J., Zeisler R., Danesi P., Kis-Benedek Gy. (1997) A Novel Technique for the Simultaneous Determination of 210Pb and 210Po using a Crown Ether. JENVRAD 37(3): 355-372.

Vrecek P., Benedik L., Pihlar B. (2004) Determination of 210Pb and 210Po in sediment and soil leachates and in biological materials using a Sr-resin column and evaluation of column reuse. Appl. Rad. Isot. 60(5), 717-723.

Wallner, G. (1997) Simultaneous Determination of 210Pb and 212Pb Progenies by Liquid Scintillation Counting. Appl. Radiat. Isot. 48, No.4, p.511-514.

Wallner, G., Irlweck, K. (1997) Determination of Lead-210 and its Progenies in Aerosol Fractions of Different Particle Sizes. Radiochimica Acta 78, p.173-176.

Wallner, G. (1998) 210Pb and its Progenies in Phosphoric Acid: Significance for Low Level Determinations Using Liquid Scintillation Counting with Extractive Cocktails. J. Radioanal. Nucl. Chem. 227 (1-2), p.121-122.

Wallner, G., Berner, A., Irlweck, K. (2002) Aerosols: Unexpected disequilibrium phenomena between airborne radioactivities of Lead-210 and its progenies Bismuth-210 and Polonium-210. Naturwissenschaften 89, 569.

World Health Organisation (WHO). 1966. Methods of Radiochemical Analysis. Geneva: WHO.

3 Conclusion

The main goal of this Thesis was to find a rapid, sensitive, cost-effective and reliable method for the separation and sequential determination of the man made radionuclide ^{90}Sr and the naturally occurring radionuclide ^{210}Pb in environmental samples.

When determining ^{90}Sr in environmental samples with higher ^{210}Pb content some authors observed impurities in the beta spectra of ^{90}Sr. In the initial stage of the work an extraction chromatography method based on the use of strontium selective resin composed of bis-t-butyl-cis-dicyclohexano-18-crown-6 in 1-octanol (also called Sr▪Spec Resin) was studied. Here bone samples with known activities of the respective radionuclides were used. A sample was dissolved in 8M HNO_3 medium and added to a column containing Sr-specific resin that retains Sr^{2+}. Strontium was eluted from the column with distilled water. ICP-MS as well as LSC spectra confirmed that ^{210}Pb was also eluted from the column together with ^{90}Sr with distilled water when the original sample contained an excessive amount of Pb over Sr. So a separation step before loading the sample onto the Sr Spec column had to be applied to eliminate the ^{210}Pb included in the sample. Several operations were tested in order to eliminate the ^{210}Pb interferences. For this purpose a standard solution containing various cations was prepared from appropriate salts to simulate the mineral composition found in animal bones. Separation of Sr from Pb was examined via different anion-exchange columns. Finally, a two-steps procedure for the separation of ^{90}Sr and ^{210}Pb in animal bones and soil samples was successfully developed. The method comprises two sequential separations. In the first step, Pb was separated from Sr and other cations on Dowex 1 x 8 (100-200 mesh) column. Subsequentlly, ^{90}Sr was purified on Sr•Spec resin: at first, Ca and the Ra isotopes were eluted with 3 M HNO_3 and then Sr was eluted with distilled water. For soil samples, an additional precipitation step for Sr preconcentration is recommended before loading the sample onto Sr▪Spec resin. With this two-steps procedure pure ^{210}Pb and ^{90}Sr spectra can be achieved. Furthermore, this method was verified on the reference sample IAEA-135 as well as on a soil profile from an

Alpine region - Naßfeld near Bdgastein - recently measured in Seibersdorf laboratory. The results for the reference sample were in excellent agreement with certified values. The same holds true for the soil profile from Naßfeld. Reference material IAEA-A-12 (animal bone) and two reindeer samples from Russia were examined for Sr and Pb content using two-steps method for Sr and Pb determination and using faster i.e. one-step SrSpec procedure for Sr determination only. ^{90}Sr results for the reference material IAEA-A-12 were within the 95% confidence interval of the certified value. Excellent agreement was found with old data gained by the “classical” method (^{90}Sr separation using fuming nitric acid and ^{210}Pb determination via ^{210}Po). Ten bone samples of animals hunted in different regions of Austria were examined by two above mentioned methods (two-steps procedure, faster SrSpec procedure). In most cases there was good correspondence between the methods, only a few samples gave differing results. All spectra were confirmed as pure ^{90}Sr spectra due to the ingrowing daughter nuclide ^{90}Y. Although the single step extraction chromatographic method with Sr▪Spec (for Sr determination only) is faster, further in this work the use of two steps procedure was favoured because the ^{90}Sr fraction is free from ^{210}Pb impurities and the ^{210}Pb activity concentration can be measured in a separate fraction.

The main sources for anthropogenic radionuclides in the environment was the global fallout from atmospheric weapons testing during the 1950s and 1960s of the last century and releases from nuclear power plants and spent fuel reprocessing plants on a local scale. After the reactor accident at Chernobyl on April 26th, 1986, Austria and especially some of its alpine regions also received atmospheric deposition from this source. Soil samples from Austria can be expected to hold contributions both from weapons test fallout and the Chernobyl accident. While ^{137}Cs is easily measured gamma spectrometrically and therefore sources of data exist, there is still a gap in the data with regard to ^{90}Sr since its radiochemical analysis is time-consuming. Therefore, the ^{90}Sr data from field studies after Chernobyl fallout are scarce and limited to lowland areas and are missing in the scale between 500 – 1700 m site altitudes. This study should complete the data set of ^{90}Sr activities for soil and bone samples to get a better understanding about the distribution of natural and anthropogenic radionuclides in environment. For this purpose also

the soil samples were examined for anthropogenic (^{90}Sr, ^{137}Cs) and natural (^{238}U, ^{232}Th, ^{40}K, ^{210}Pb) radionuclides.

The soil samples were collected from the eastern part of the Alps in Styria (Rettenegg, 860 m; Kaltenegg, 1000 m), the southern part of the Central Alps in Carinthia (Ossiacher Tauern, 680 m; and Saualpe, 1895 m; a mountain ridge with Mirniger Alm, 1530 m, on its western slope) and from the Central Alps in Salzburg (Mariapfarr region, 1340 m; 1530 m and 1786 m). Additionally one sample from the midle part of Slovakia (Prievidza, 600 m) was collected. The top 6 cm of the soil surface were taken for the analyses. The activity concentrations of anthropogenic ^{137}Cs, and natural ^{40}K, ^{238}U and ^{232}Th in powdered soil samples were evaluated gamma spectrometrically. ^{238}U and ^{232}Th were determinated indirectly using daughters (^{226}Ra, ^{214}Pb, ^{214}Bi) and (^{228}Ac, ^{212}Pb, ^{208}Tl), respectively. ^{137}Cs and ^{40}K were determinated directly using their single gamma lines. From obtained specific activities of ^{40}K, ^{238}U and ^{232}Th the absorbed dose rates in air (nGy.h^{-1}) 1m above ground and annual effective dose rates outdoors using units mSv.y^{-1} were calculated. The absorbed dose rates in air 1m above ground and annual effective dose rates outdoors for studied soils from Austria as well as for one sample from Slovakia were within the values published by UNSCEAR compilation.

The next task was the determination of the activity concentrations of ^{90}Sr and ^{137}Cs in soil samples and of ^{90}Sr in bones of deer animals hunted in appropriate regions. The data of these anthropogenic nuclides were compared to the activity concentration of the naturally occurring ^{210}Pb. ^{90}Sr and ^{210}Pb content in soil samples was determined using a two-steps procedure where oxalate and hydroxide precipitations were provided. In this work the correlation between the activity concentration of ^{90}Sr and ^{137}Cs in soil samples and site altitude was studied. From the activity ratio ^{90}Sr/^{137}Cs the source of contamination (weapon tests fallout and/or reactor accident in Chernobyl) can be derived.

The activity concentrations of the global fallout nuclides showed a correlation with the site altitude, as the nuclides are mainly washed out by wet precipitation, which is higher in the mountains. Principally the same holds true for the deposition of Chernobyl fallout, but the regional variations are much

larger in this case, as precipitation occurred only in some regions during the critical time-span when the radioactive cloud passed Austria. The highest ^{90}Sr and ^{137}Cs values were found on the Saualpe / Mirniger Alm, probably because of rain reported in this site during the days after the Chernobyl accident. The corresponding $^{90}Sr/^{137}Cs$ ratio (0.08-0.09) clearly indicates a large contribution from Chernobyl. The lowest ^{90}Sr and ^{137}Cs values were measured in Kaltenegg (with a ratio of 0.1); a few kilometers apart in Rettenegg the respective data were higher with a lower $^{90}Sr/^{137}Cs$ ratio (0.05) indicating again a higher contribution from Chernobyl, probably due to local rainfall. The samples from Mariapfarr generally showed lower activity levels in the surface layers together with clearly higher $^{90}Sr/^{137}Cs$ ratios. Here the portion of nuclides from the global fallout is higher since after the Chernobyl accident the weather was dry. The Mariapfarr sampling sites were all on the southern slope of one specific mountain ridge in the Niedere Tauern, showing very clearly the site altitude dependence of the activity concentrations. Another activity / site altitude correspondence (with comparably higher activity concentrations) can be found for the sites in Carinthia with higher contributions from Chernobyl.

^{210}Pb is a naturally occurring radionuclide and its content in soil depends on the geological conditions of appropriate region. All the samples stem from gneiss areas, therefore the variation of the activity concentrations is rather low (30-100 $Bq.kg^{-1}$).

Additional to soil profiles, bone samples of deer from the sites where the soils were collected and their ^{90}Sr and ^{210}Pb concentrations were measured. The animals stem from sites with altitudes between 150 and 1530 m a.s.l.. ^{90}Sr activity concentrations in bone ash samples were compared to the data of the respective soil samples to study the soil to bone transfer factors (ratio activity concentration in bone ash to that in soil) for ^{90}Sr and ^{210}Pb. The transfer factor for ^{90}Sr was found between 1.2 and 3.8. These values are only a rough estimation, as number of samples was low and animals of different age were investigated. ^{210}Pb levels were similar in animal bone ash and soil (transfer factor between 0.4 and 1.2). This reflects the fact that due to its chemical similarity with Ca, ^{90}Sr is more easily transported to the bones than ^{210}Pb. Aditionally, desired values of ^{90}Sr for all bone samples

examined during this work which were collected all over Austria were used to study dependence of animal age and site altitude to ^{90}Sr content.

Generally, a direct proportional correlation between the activity concentration of ^{90}Sr and ^{137}Cs in soil samples and site altitude was found. Also the ^{90}Sr content in deer bones corresponds with the site altitude. The ^{90}Sr values in deer bones are directly proportional to the values in the respective soil samples and also to the age of the animals. The activity concentration/altitude correlation can be seen more clearly if only animals of the same age are considered, as the ^{90}Sr content increases also with the age of the animal. Compared to older literature, ^{90}Sr values in deer bones presented in this work were lower, probably indicating a decreased bioavailability of ^{90}Sr bound to soil particles.

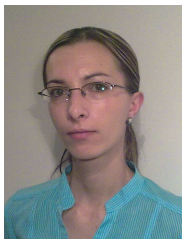
The 3M Empore Sr Rad disks were developed for ^{90}Sr separations from liquid samples. In this work the simple procedure for determination of ^{90}Sr in bone samples using 3M Empore Sr Rad disks was investigated. After leaching of bone samples with concentrated nitric acid, hydroxide and oxalate precipitations were utilized followed by separation using disk. The applicability of the 3M Empore Sr Rad disk method to determine the ^{90}Sr in bone samples was verified using reference sample IAEA-A-12 (bone ash).

The soil sample from midle part of Slovakia (Prievidza, 600 m) showed lower ^{90}Sr and ^{137}Cs activity levels in the surface layers with clearly higher ^{90}Sr/^{137}Cs ratios. The portion from Chernobyl fallout is aproximatelly 50 % due to the favourable weather during the days after the Chernobil accident. Two bone samples from this region were examined for ^{90}Sr and ^{210}Pb content. For this purpose the two-step procedure and Empore disks were used. Finally, the teeth of my son Peter Walla were investigated for ^{90}Sr content. The short Sr Spec method was used because of limited amount of sample. Peter Walla was born on 4th April 2003 in Handlova (Slovakia). He lived the first 2 years of his life in the region where the soil and bone samples from Slovakia were collected. Since 2005 he has lived in Vienna (Austria). The teeth were collected in the period of September to November 2009. The activity concentration of ^{90}Sr was found to be 27.9 ± 2.9 Bq.kg^{-1} (reference date: 1st September 2005).

For the identification of an alpha-emitter as ^{210}Po (discrimination against ^{239}Pu) in urine samples three short separation methods using the extractive cocktail Polex®, the Sr·Spec®resin and the Sr Rad disk® were developed. All three methods extract Po with an efficiency of more than 90%, while Pu is not extracted into POLEX® and retained neither on the Sr·Spec® column nor on the Sr Rad Disk®. Only very little handling of the sample is necessary, and the results are available within a few hours latest. Therefore these fast methods are well suited in emergency situations when measurements of incorporated activities are a prerequisite for further decisions.

4 CURRICULUM VITAE

PERSONAL DATA



Name	***Gabriela Wallova***
Address	Buchengasse 56/40 1100 Wien Austria
Phone	+43-681-10757065
E-mail	gabriela.wallova@univie.ac.at
Birth date	18. September 1981
Citizenship	Slovakia
Family status	married (2002), one son (*2003)

EDUCATION

1988-1996	Elementary School, Chrenovec-Brusno (Slovakia)
1996-2000	Grammar School, general section, Handlova (Slovakia)
2000-2004	B. Sc. in Chemistry, Specialization Nuclear Chemistry, Department of Nuclear Chemistry and Radioecology, Faculty of Natural sciences, Comenius University Bratislava, (Slovakia)
2002-2003	Interruption of the study due to maternity leave
2004-2006	MSc. in Chemistry, Specialization Nuclear Chemistry, Department of Nuclear Chemistry and Radioecology, Faculty of Natural sciences, Comenius University Bratislava, (Slovakia)
2009-2010	RNDr. in Chemistry (external study), Specialization Nuclear Chemistry, Department of Nuclear Chemistry and Radioecology, Faculty of Natural sciences, Comenius University Bratislava, (Slovakia)
2006-2011	Doctoral study at the University of Vienna, Austria

Languages

Slovak (mother language)
Czech
English
German

Scientific skills

Experience with LSC (Liquid Scintillation Counting), Alpha and Gamma spectrometry, Proportional counting, ICP-MS (Inductively Coupled Plasma Mass Spectrometry), AAS (Atomic Absorption Spectrometry)

Performance and development of radioanalytical methods for determination of natural and anthropogenic radionuclides in environmental samples.

Miscellaneous

Membership in Austrian Chemical Society
Driving license of type A, B