Development and application of an analytical strategy for the determination of ^{232}Th and ^{228}Th in ivory based on the combined use of inductively coupled plasma mass spectrometry and α-spectrometry

Dissertation

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Development and application of a method for ivory dating by analyzing radioisotopes to distinguish legal from illegal ivory

Andreas Schmidberger, Bernhard Durner, David Gehrmeyer and Robert Schupfner

Forensic Science International (2018) 289: 363-367.

Abstract

The age determination of elephant ivory provides necessary and crucial information for all criminal prosecution authorities enforcing the Convention on International Trade in Endangered Species of Wild Fauna and Flora. The knowledge of the age of ivory allows to distinguish between pre-convention, hence legal material and ivory deriving from recent, illegal poaching incidents. The commonly applied method to determine the age of ivory is radiocarbon dating in the form of bomb pulse dating, which however will fade out soon. This work provides an enhancement of the radiocarbon dating method by supplementary determination of the isotope profile of 90-Sr and the two thorium isotopes 228-Th and 232-Th. This combined analysis allows for a precise and unambiguous age determination of ivory. We provided calibration curves for all involved radionuclides by analyzing ivory samples with known age and investigated a new method for the extraction of strontium from ivory.

Development of an analytical strategy for the determination of ^{228}Th and ^{232}Th in ivory based on the combined use of ICP-MS and α-spectrometry

Andreas Schmidberger, Robert Schupfner and Frank-Michael Matysik

Journal of Radioanalytical and Nuclear Chemistry (2018) 318: 2007-2011.

Abstract

Elephants are endangered due to the value of their ivory tusks. Therefore, a reliable method for age determination of ivory is of interest for the law enforcement against elephant poachers. The ratio of the specific activities ^{228}Th/^{232}Th can be used for the age assessment of ivory. In this report, the combination of two complementary detection techniques, namely inductively coupled plasma - mass spectrometry (ICP-MS) and α-spectrometry, for the determination of ^{228}Th and ^{232}Th in ivory is presented. Using ICP-MS in addition to α-spectrometry, the uncertainty of the ^{232}Th determination could be reduced significantly, which enabled a more accurate and effective ivory dating.

Monitoring the equilibration of ^{228}Th and decay products over time after extraction from ivory

Andreas Schmidberger and Robert Schupfner

Journal of Radioanalytical and Nuclear Chemistry (2019) 320: 139-143.

Abstract

The worldwide population of elephants shows a rapid decline due to trafficking of ivory. Hence, a method is needed for the age determination to distinguish legal from illegal ivory. The analysis of ^{228}Th and ^{232}Th in ivory can be used for this purpose. This study provides a technique for the analysis of ^{228}Th in ivory. The thorium was extracted from ivory and measured after various time periods applying α-spectrometry until a secular radioactive equilibrium between ^{228}Th and its decay products was established. An equilibration period of 32 days was found. The uncertainty of the determination of the activity of ^{228}Th could be reduced by integrating the counts of the equilibrated decay products into the determination process.

Miscellaneous

CE-UV/VIS and CE-MS for monitoring organic impurities during the downstream processing of fermentative lactic acid from second-generation renewable feedstocks

Hendrik Laube, Frank-Michael Matysik, Andreas Schmidberger, Kerstin Mehlmann, Andreas Toursel and Jana Boden

Journal of Biological Engineering (2016) 10: 1-11.

Abstract

During the downstream process (DSP) of bio based bulk chemicals, organic impurities, mostly residues from the fermentation process, have to be separated in order to gain a pure and ready-to-market chemical. In this study, capillary electrophoresis (CE) was investigated for the non-targeting DSP monitoring of organic impurities and the simultaneous quantitative detection of lactic acid (LA) during the purification process of fermentatively produced LA. The DSP incorporated 11 separation units, ranging from filtration, adsorption and ion exchange to electrodialysis and distillation. Furthermore a variety of 15 different second generation renewable feedstocks were processed into LA. The identification of organic impurities was established through spiking and the utilization of an advanced CE-MS system. While 53 % of the organic impurities were efficiently removed by the bipolar electrodialysis one impurity, pyroglutamic acid, divorced itself from separation. It has been proven that its presents disturbed the polymerization reaction of LA into poly LA.

Characterization of a laboratory-constructed miniaturized device for fast CE measurements with contactless conductivity, amperometric, and mass spectrometry detection

Andreas Schmidberger, Sebastian Piendl, Jonas Mark and Frank-Michael Matysik

Monatshefte für Chemie – Chemical Monthly (2017) 148: 1661-1665.

Abstract

In the recent years, attention for fast separation of all kind of samples in combination with automated systems has increased. On that account we designed and constructed a miniaturized capillary electrophoresis system, which can achieve fast separations, due to short capillary length and high electric field strength. An integrated and exchangeable autosampler unit, which can be loaded with 19 samples at once, allowed high throughput measurements with small sample volumes down to 30 µL. The design of the device enables the implementation of various detectors. The aim of this work was the analytical characterization of this device in combination with mass spectrometry, amperometric and capacitively coupled contactless conductivity detection. Hydrodynamic and electrokinetic injections were carried out with different injection parameters. Different model systems for each detection technique were used, to test the performance of the device, concerning speed of separation, precision, resolution and sample throughput.

Declaration of collaboration

The upmost part of the theoretical and experimental work presented in this thesis was done by the author. Nevertheless, some of the work was done in cooperation with other researchers. Fulfilling § 8 Abs. 1 Satz 2 Punkt 7 of the "Ordnung zum Erwerb des akademischen Grades eines Doktors der Naturwissenschaften (Dr. rer. nat.) an der Universität Regensburg vom 18. Juni 2009, this chapter describes the form and content of the individual cooperations. The statements are structured according to the subdivisions of the chapter "4. Results and discussion".

4.1 Age determination of young ivory to continue the calibration curves for the radionuclides ^{14}C, ^{90}Sr and $^{228}Th/^{232}Th$

The ivory samples No. 11-20 were solely analyzed by the author. The samples No. 1-10 were analyzed as part of a cooperation. Concerning these samples, the full analysis of $^{228}Th/^{232}Th$ was done by the author alone. The analysis of ^{14}C was done by the author and Bernhard Durner. The analysis of ^{90}Sr and the development of the new extraction method of ^{90}Sr were done by Bernhard Durner. The author, Bernhard Durner, Dr. Robert Schupfner and David Gehrmeyer wrote the manuscript for publication. Dr. Robert Schupfner supervised the work.

4.2 Long-term study on the change of the ratio $^{228}Th/^{232}Th$ in ivory over time

The experimental work was performed solely by the author. Dr. Robert Schupfner supervised the work.

4.3 Development of an analytical strategy for the determination of ^{228}Th and ^{232}Th in ivory based on the combined use of ICP-MS and α-spectrometry

The experimental work was performed solely by the author. Dr. Robert Schupfner and Prof. Dr. Frank-Michael Matysik supervised the work.

4.4 Monitoring the time dependent equilibration of ^{228}Th and decay products in ivory via α-spectrometry

The experimental work was performed solely by the author. Dr. Robert Schupfner supervised the work.

4.5 Development of a method for yield determination of radioanalytical analysis via ICP-MS

The experimental work concerning the thorium extraction from ivory and all ICP-MS measurements were performed solely by the author. The experimental work of the extraction of uranium from aerosol filter was done by Helga Gammel. Dr. Robert Schupfner supervised the work.

1. Introduction

The humanity faces the extinction of various animal and plant species. There is both natural extinction and human-induced extinction, which exceeds the former one by several orders of magnitude [1]. The extinction affects the whole range of species diversity, such as mammals, insects and marine life. The extinction rates explode, fueled by the climate change [2], the destruction of the natural habits and the exploitation of animal products [3]. Even the species that is most associated with the African wildlife is on the verge of extinction. A continent-wide survey study revealed the massive decline of the African elephant (*Loxodonta Africana*) [3]. The population of the African elephant was estimated at a very low number of 350,000 [3]. The decline is ongoing with an annual continent-wide decrease of 8% [3]. This decline rate is caused by the ivory industry, which declares the elephants as targets to be killed for economic purpose. In 1975, the Convention on International Trade in Endangered Species of Wild Fauna and Flora was signed, which should ensure the survival of various animal species and plants [4]. The Convention is currently signed by 183 parties, which shows a widespread acceptance and that the issue is being taken seriously. The Convention strictly regulates the trade of ivory and each country implements the content of the Convention in its own way. In Germany, the trade of ivory deriving from an elephant killed after the year 1976, is prohibited. However, the poaching industry and the associated ivory trafficking is still ongoing and a threat for the elephant population. The distinction between legal ivory, which still may be traded, and illegal ivory, which was taken from the animal after the year 1976 is crucial for the enforcement of the Convention and the survival of the elephants. There is a need for a reliable and robust method for the age determination of ivory to distinguish legal and illegal ivory, which serves the criminal prosecution as tool against ivory trafficking and elephant poaching.

The variety of dating techniques is huge and the suitable technique depends on the nature and the actual age of the sample [5-8]. Since the radioactivity is a time dependent phenomenon, a dating method including the analysis of radionuclides [9-11] seems straightforward. The middle of the 20th century was marked by the test phases and the use of nuclear bombs [12]. This intervention in the natural isotope ratios of the environment enables a dating method applicable for the purpose of ivory dating [13, 14]. The analysis of the isotopes ^{14}C, ^{90}Sr and the ratio of the activity concentrations of ^{228}Th and ^{232}Th enables the unambitious age determination of ivory using a combined method for all mentioned isotopes [14]. Since all these isotopes show radioactive properties [15-17], the analysis via radiometric detection techniques provides reliable activity determinations. Besides the radiometric approaches, the inductively coupled plasma mass spectrometry (ICP-MS) provides a versatile and powerful technique for isotope analysis [18-20]. The combination of radiometric detection techniques and ICP-MS for the determination of radionuclides in a variety of matrices [21] and for various analytes [22] is described in the literature. Concerning the long-lived isotopes, such as ^{232}Th, the ICP-MS seems to be a promising addition to the pure radioanalytical approach. The benefit of the combination of both detection principles for the determination of the ratio ^{228}Th/^{232}Th in ivory is the low uncertainty, which would not be achievable with a solely radiometric measurement. Hence, the dating uncertainty of ivory material via the combined detection principles could be greatly reduced.

The following aspects were the central ideas of this thesis:

- Extension of the calibration curves for the time dependent activities for the isotopes ^{14}C, ^{90}Sr and the ratio ^{228}Th/^{232}Th in ivory – acquisition and analysis of suitable ivory samples
- Validation of the expected changing of the ratio ^{228}Th/^{232}Th in the first years after death of the elephant by the analysis of chosen ivory material after time intervals
- Improvement of the determination uncertainty of ^{232}Th by integrating ICP-MS measurements in the analytical procedure
- Improvement of the determination uncertainty of ^{228}Th by an extended evaluation procedure including the decay products of ^{228}Th
- Application of the ICP-MS for the means of yield determination of the thorium analysis in ivory

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2. Background and theory

2.1 Fundamentals of age determination

2.1.1 Techniques for age determination

The information about the age of all kind of materials is crucial for various analytical determination processes. The age of a sample is of interest, since the time after sample drawing can change the content of the analyte. The age determination itself can be the analytical question as well. The method of choice for age determination depends on the nature of the sample [1]. The diversity of sample matrices is huge. Minerals [2], fossils [3], art objects [4], human bones [5] and animal tissue, such as pelt [6], bone [7], horn [8] and ivory [9] are targets for age determination. In general, each sample can be analyzed for dating purposes. The purpose is in many cases the historical classification of fossils, minerals and art objects. The age determination of animal residues can give an impression about the evolution of the specimen population in a geological region. As discussed in the introduction, the purpose of age determination is also connected to juristic consequences. There is a huge demand for animal products due to naturopathy. This demand threatens the survival of the species. The survival of the species should be ensured by laws, which prohibit the animal hunting. The enforcement of the laws causes a general demand for reliable age determination techniques.

The application of an age determination technique depends on various factors. The choice depends on the possible age window and the age itself. Hence, a technique can be suitable to determine the formation century of a mineral in an age range of 100,000 years, but the technique fails if the formation was just years ago. Some of the common techniques operate in an age window of days or even hours, such as the age analysis of a dead body [10] in a criminal incident. These can be techniques, which only determine the decay status of the body without further chemical analysis. Indicators are the temperature of the body or the infection by insects [10]. Other techniques operate in an age window of several thousand years, as it is the case for fossils [11]. The composition of the sample is also crucial for the choice of a technique. Since the radiocarbon dating bases on the carbon content of the sample, the carbon content should exceed a certain limit. The applied methods differ for each sample and can be differentiated between destructive and non-destructive procedures. It seems convenient to apply a destructive method, such as radiocarbon dating initiated by incineration, to a sample which is not of higher financial, historical or emotional value. Other kinds of samples, such as paintings, virtues and decoration objects, should be analyzed via non-invasive dating methods, or if it cannot be avoided, the amount of required sample mass should be as low as possible. A selection of age determination methods is shown in Table 2.1 to demonstrate the diversity of the techniques.

Table 2.1: Techniques and corresponding applications for age determination.

Age determination technique	**Application**	**Reference**
Radiocarbon dating	All samples containing carbon	[12], [13]
Potassium-argon dating	Rocks and minerals	[14], [15]
Luminescence dating	Minerals	[16], [17]
Amino acid dating	Biological samples	[18], [19]
Bomb curve dating	Animal tissues	[20], [21]
Electron spin resonance dating	Human tooth remains	[22], [23]

Each technique analyzes different time-dependent properties of the compounds. The amino acid dating technique, which was investigated by Bada et. al [18], is based on the change of biological molecules after death. The natural L configuration of amino acids in former living cells shifts to the D configuration with passed time after death [19]. This phenomenon is used in the fields of paleontology, archaeology or forensic science. Requiring biological molecules, the amino acid dating is only applicable on residues of former living animals or humans.

Techniques such as luminescence dating and electron spin resonance dating are based on the exposition of samples to natural radioactivity. The longer the exposition of the sample to radioactivity the higher the signals obtained by these methods. The electron spin resonance dating is applicable to newly formed material as well as material older than 200,000 years [23]. This makes the electron spin dating more flexible as the radio carbon dating, which fails for too long or too short age ranges.

The best-known dating methods are based on the radioactive decay, such as radiocarbon dating, bomb curve dating and potassium-argon dating. The radiocarbon dating represents this subgroup of techniques for age determination. It became famous by contributing to the successful age determination of the human remains of the iceman Ötzi [24]. These methods are based on the natural radioactivity of the samples, which decreases after time. Using the common mathematical operations, the age or the death time of the sample specimen can be calculated. The long traceability and longevity of some radionuclides guarantees a successful age determination even million years [25] after the formation of the respective object. The artificial isotopes, which were generated by humanity, can be used as well for the purpose of age determination. Since the time period of the emission of artificial radionuclides into the atmosphere is well known, the age window of a sample containing artificial isotopes can be defined precisely. The emission of artificial isotopes took place in the middle of the

20th century, meaning the application of this dating technique is only suited for samples after 1960 [21]. The dating techniques, which are based on radioactivity are described further in the next chapter.

2.1.2 Age determination via radionuclides

Radioactive nuclides show an unpredictable and completely independent nuclear reaction, accompanied by the emission of a particle and energy. The nucleus of the nuclide changes as a result. The most common radioactive decays are the α-, β- and γ-decay. The number of decays in a time period (t) is proportional to the number of present nuclides (N). Equation 1 shows the relation.

$$-\frac{dN}{dt} = \lambda \cdot N = A \tag{1}$$

A is the activity ([1/s] or [Bq] = Becquerel) and λ is the decay constant [1/s] of the nuclide. Equation 2 and 3 show the result of integrating Equation 1, whereas N(t) is the number of nuclides after passed time t, N_0 is the number of nuclides at t = 0, A(t) is the activity after the passed time t and A_0 is the activity at t = 0.

$$N(t) = N_0 \cdot e^{-\lambda t} \tag{2}$$

$$A(t) = A_0 \cdot e^{-\lambda t} \tag{3}$$

The decay constant λ can be transformed to the half-life ($T_{1/2}$), which represents the time after which half of the original nuclides are decayed. The half-lives of all radionuclides are well described in the literature. The transformation of λ to $T_{1/2}$ is described in Equation 4.

$$T_{1/2} = \frac{ln2}{\lambda} \tag{4}$$

The diversity of decays and decay properties is huge. Table 2.2 shows selected radionuclides and their decay parameters, namely the type of decay, the decay energy, the half-life and the percentage share of the isotope in the total element amount.

Table 2.2: Chosen radionuclides with corresponding decay parameters adapted from [26].

Radionuclide	**Decay**	**Energy**	**Half-life**	**%***
^{3}H	β	0.019 MeV	12.33 a	10^{-15}
^{14}C	β	0.156 MeV	5730 a	$< 10^{-9}$
^{32}P	β	1.711 MeV	14.26 d	Synthetic
^{212}Bi	α β	6.207 MeV 2.254 MeV	60.55 min	Synthetic
^{244}Pu	α	4.666 MeV	$8.0 \cdot 10^{7}$ a	≈100
^{238}U	α	4.270 MeV	$4.5 \cdot 10^{9}$ a	99.3
^{232}Th	α	4.083 MeV	$1.41 \cdot 10^{10}$ a	≈100

* Percentage share of the isotope in the total element amount. Synthetic elements are decay products of decay series and are normally not present in the environment.

Radionuclides exist in all variations concerning the decay properties. There are solely α-emitters as well as solely β-emitters and radionuclides who show both decays, such as ^{212}Bi. The half-life diversity is also huge from an hour (^{212}Bi) over days (^{32}P) to years (^{3}H). ^{3}H and ^{14}C have a very small natural occurrence in the environment in contrast to ^{224}Pu and ^{232}Th, which represent roughly 100% of their occurrence in the environment.

The radioactive decay, which is the most important one in this project, is the α-decay. The process of an α-decay of an unspecified radionuclide is described in Equation 5.

$$ {}^{y}_{x}A \rightarrow {}^{y-4}_{x-2}B + {}^{4}_{2}He + \Delta E \tag{5}$$

The nuclide A with the atomic number x and the neutron number y decays by emitting an α-particle, which is a helium core with the atomic number 2 and the neutron number 4, and is transformed into the nuclide B with the atomic number x-2 and the neutron number y-4. The kinetic energy of the α-particle ΔE can be calculated by the mass difference ΔM (Equation 6).

$$ m\left({}^{y}_{x}A\right) - \left(m\left({}^{y-4}_{x-2}B\right) + m\left({}^{4}_{2}He\right)\right) = \Delta M \tag{6}$$

This mass difference is the equivalent of the kinetic energy of the emitted α-particle and is specific for the α-decay of the radionuclide A. The energy and the amount of decays give qualitative information about the identity of the nuclide and quantitative information about the activity of the nuclide, respectively. Both values are crucial for the purpose of age determination.

Most radiometric techniques of age determination are based on the fact that the activity of an object is dependent on passed time (Equation 3). The procedure of the radiocarbon dating method is used in the following to describe the procedure of the age determination via radionuclides. Before 1950, the ratios of stable and unstable elements (e.g. $^{14}C/^{12}C$) were constant in the environment. Reason for that was the equilibrium between the decay and the formation of the isotope ^{14}C. The unstable ^{14}C was formed by the interaction of a neutron (cosmic radiation [27]) with stable ^{14}N [28]. This ratio entered the body of a living being via the typical ingestion pathways, such as eating, drinking and breathing [29]. The ratio was continuously supplied until the death of the animal or plant. Since then, only the decay of the unstable isotope continues and the activity dropped with passed time. Using the Equations 3 and 4, the age of the animal can be calculated by determining the ^{14}C activity. This method of radiocarbon dating uses the natural activity in the environment. Since 1950 [30], artificial isotopes were released into the atmosphere and the natural equilibria, such as the ratio $^{14}C/^{12}C$, were disturbed. The influence on the natural isotope ratio and the resulting opportunities for age determination is discussed in the next chapter.

2.1.3 Age determination of ivory using bomb curves

Besides the natural radioactive isotopes in the environment, whose content is self-regulated by cosmic radiation, the human kind strongly interfered in these equilibria by testing atomic bombs [31]. The decay products of these nuclear reactions were released in the environment accompanied by a huge number of neutrons. These neutrons induced nuclide reactions and increased the percentage share of radioactive isotopes in the environment of various elements [32, 33]. Since the era of the atomic bomb tests was between 1960 - 1970, the peak of the radionuclide increases can be found in this decade. Figure 2.1 shows the bomb curve for the atmospheric ^{14}C share in the second half of the 20th century.

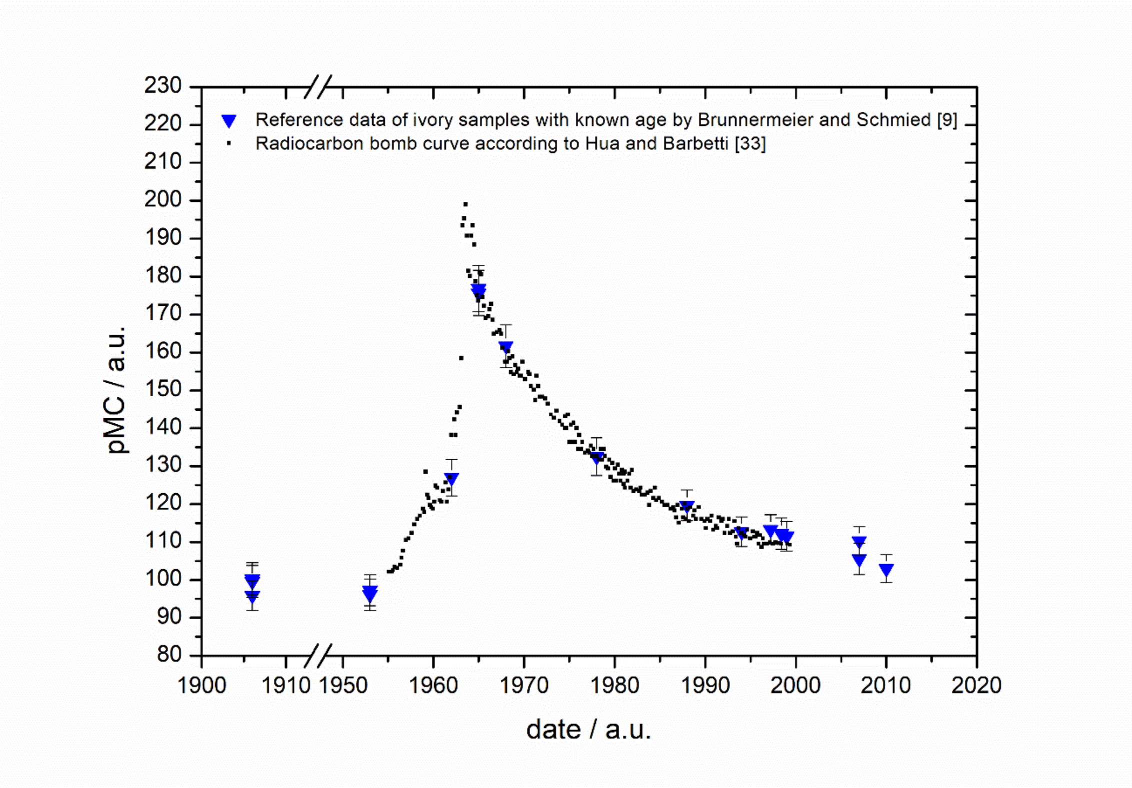

Figure 2.1: Bomb curve of ^{14}*C in the second half of the 20th century. Comparison of atmospheric* ^{14}*C (adapted from [33]) with* ^{14}*C in ivory (adapted from [9]).*

A bomb curve visualizes the increase of a radionuclide content in the environment due to the atomic bomb tests. The ^{14}C content is calculated as percentage modern carbon (pMC) [34]. The value before the bomb test phase was roughly 100 pMC and did not change until the bomb tests. Due to the released neutrons, an increase of the pMC value took place, which had a maximum in 1965 with a value of roughly 200 pMC. After the bomb tests stopped, the value dropped and assimilated with passed time to the value before the bomb tests. The studies of Brunnermeier and Schmied [9] showed that the share of ^{14}C in the atmosphere could be recovered in ivory tissue. This accordance is the base of the ivory age determination via bomb curve dating. A radiocarbon analysis of ivory tissue is conducted and the result is compared with the curve in Figure 2.1. Considering the shape of the curve, there are in most cases two potentially correct age ranges with equal possibility. The age determination is ambiguous. Since the solely radiocarbon analysis is not enough, a further radio analysis must be done to determine the correct age range.

The radionuclide ^{90}Sr seems to be a useful indicator for the age of ivory. ^{90}Sr is an artificial isotope, which is normally not present in nature, but was released as fission product [35] in the atmosphere due to the atomic bomb tests. The bomb curve for ^{90}Sr in the second half of the 20th century is depicted in Figure 2.2.

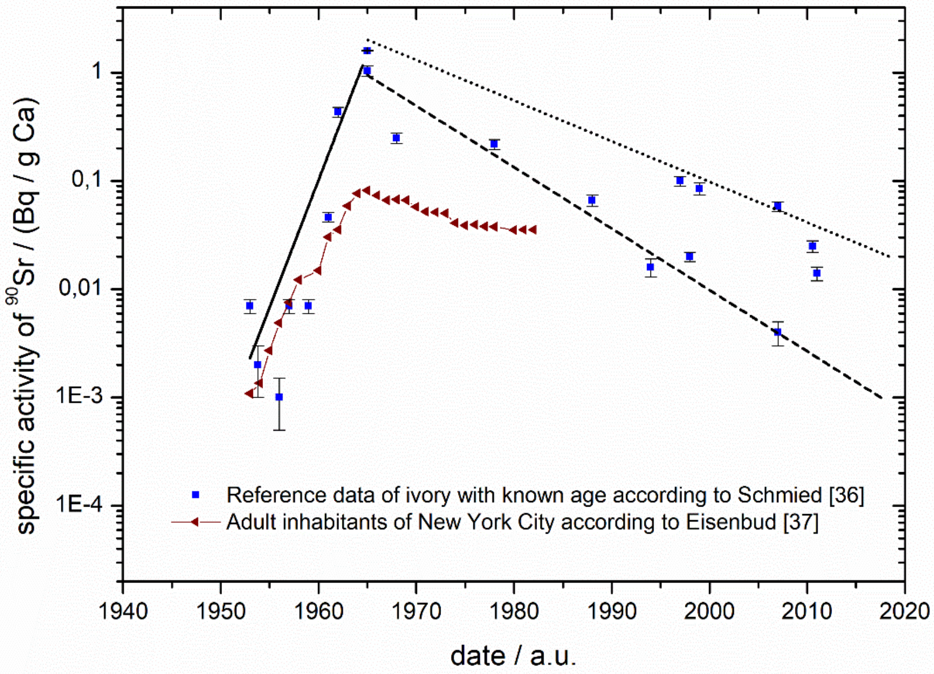

Figure 2.2: Bomb curve of ^{90}Sr. Comparison of ^{90}Sr content in adult bones (adapted from [37]) and ivory (adapted from [36]).

The ^{90}Sr bomb curve in Figure 2.2 shows a similar trend as the ^{14}C curve in Figure 2.1. There is a maximum of ^{90}Sr content in human bones as well as in ivory in the year 1965. The specific activity of ^{90}Sr in ivory decreases after 1965. This means that if a significant ^{90}Sr content is found in ivory, the elephant had to be alive after 1952, because only after this date the artificial ^{90}Sr was present in the atmosphere and could be incorporated by the elephant. In many cases, this information eliminates one possible time frame resulting from the radiocarbon determination, but there are some cases, which need even more analytical evidence. Furthermore, the increased atomic bomb related isotope levels in the environment of ^{14}C and ^{90}Sr will decrease with passed time and the differentiation of very new (illegal) and very old (legal) ivory will not be possible anymore. There is a demand for an age determination technique, which is independent of the bomb tests.

2.2 Determination of the activity concentration ratio ^{228}Th/^{232}Th for the purpose of age determination in ivory

The age determination of ivory via ^{14}C and ^{90}Sr works reliable but since the half-life of ^{90}Sr is 28.79 years [26], roughly 75% of the ^{90}Sr released by the atomic bombs is already decayed and the limit of detection of ^{90}Sr will be questioning the usability of the ^{90}Sr determination for ivory dating in the future. There is a demand for an approach, which does not base on the atomic bomb fallouts, but shows a time-related resolution over the last decades. Two isotopes of thorium were chosen as a support for the ^{14}C and ^{90}Sr dating technique. Thorium is omnipresent in all silica-based types of sand or rocks due to its lithophile behavior [38] and was found in a sufficient amount in ivory. Thorium shows a variety of isotopes. All relevant thorium isotopes concerning this thesis are shown in Table 2.3.

Table 2.3: Overview of thorium isotopes in this work. Values adapted from [26, 39].

Isotope	Decay energy / MeV	Half-life	Determination via	Relevance
^{227}Th	5.757 MeV, 6.038 MeV	18.68 d	α-spectrometry	Yield tracer
^{228}Th	5.423 MeV	1.91 a	α-spectrometry	Dating
^{229}Th	4.846 MeV, 4.902 MeV	7340 a	α-spectrometry	Yield tracer
^{230}Th	4.688 MeV	75380 a	α-spectrometry	-
^{232}Th	4.083 MeV	$1.41 \cdot 10^{10}$ a	α-spectrometry / ICP-MS	Dating

The elephant is incorporating thorium via the food chain and the thorium is stored in the ivory tusk. The relevant isotopes for the age determination are ^{228}Th and ^{232}Th. These isotopes are part of the 4n decay series [26], which is depicted in Figure 2.3.

$$^{232}\mathrm{Th} \xrightarrow[1.41 \cdot 10^{10}\ \mathrm{a}]{\alpha} {}^{228}\mathrm{Ra} \xrightarrow[5.7\ \mathrm{a}]{\beta} {}^{228}\mathrm{Ac} \xrightarrow[6.15\ \mathrm{h}]{\beta} {}^{228}\mathrm{Th} \xrightarrow[1.91\ \mathrm{a}]{\alpha} \ldots$$

Figure 2.3: First four decays of the thorium decay series. Values adapted from [26, 39].

Figure 2.3 shows that the thorium content and the ratio ^{228}Th/^{232}Th depends not only on the thorium incorporation of the elephant but also on the incorporation of ^{228}Ra, which decays to ^{228}Th over ^{228}Ac. Depending on the ^{228}Ra activity at the time of death of the elephant, the ratio ^{228}Th/^{232}Th in ivory shows an increase in the first years after death of the elephant [40]. After roughly 40 years, when the ^{228}Ra is mostly decayed, the ^{228}Th is only formed by ^{232}Th and the ratio ^{228}Th/^{232}Th becomes one. Figure 2.4

shows a calibration curve calculated from $^{228}Th/^{232}Th$ ratios, which were obtained by the analysis of independently dated ivory.

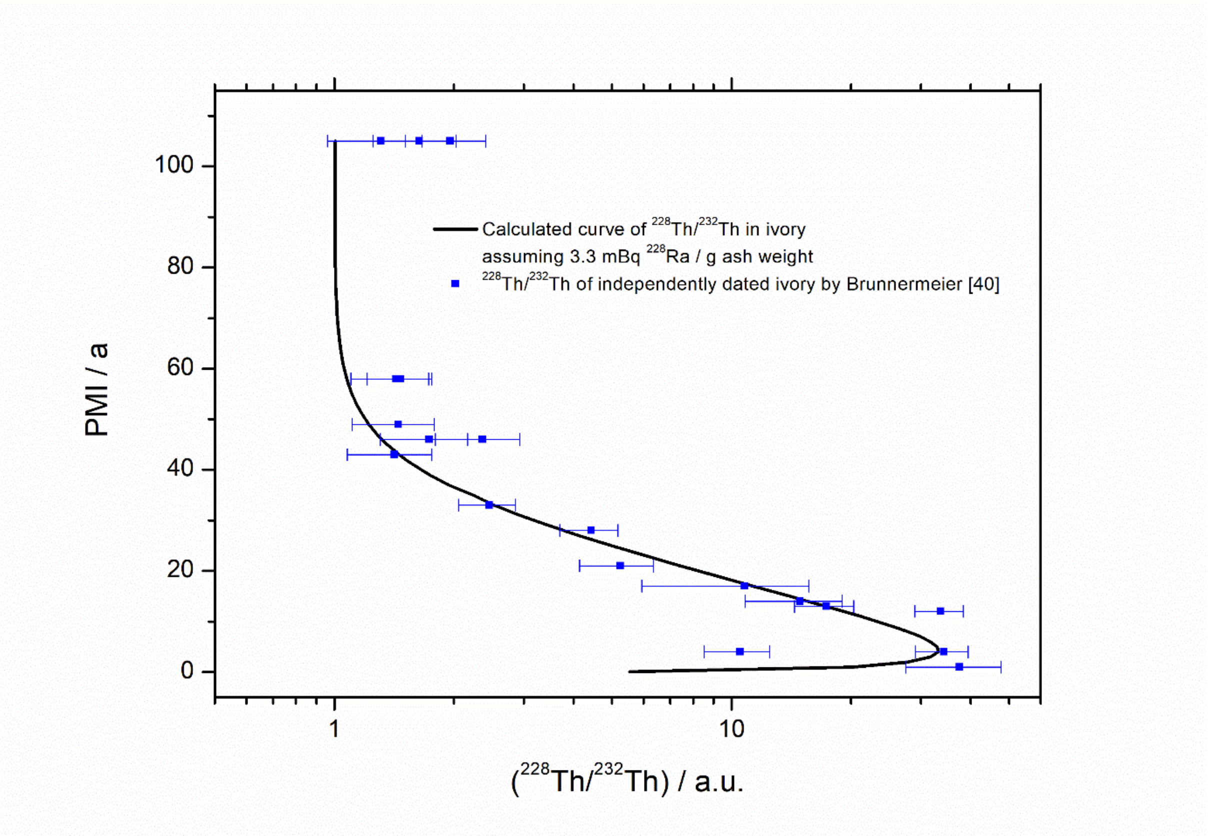

Figure 2.4: Reference values of the ratio of the activity concentrations of ^{228}Th and ^{232}Th in ivory with known age. Values adapted from [40]. PMI = Post mortal interval.

The time resolution is given as the post mortal interval (PMI). This is the time difference between analysis and death of the elephant. The theory about the ratio changing is in good accordance with the measurements made by Brunnermeier [40]. The ratio $^{228}Th/^{232}Th$ shows an increase directly after death of the elephant and a value of one after roughly 40 years. The fit curve in Figure 2.4 is a calculated curve, which represents the ratio $^{228}Th/^{232}Th$, assuming a ^{228}Ra activity of 3.3 mBq per gram ivory ash after death of the elephant. The value 3.3 mBq per gram ivory ash was chosen because it provides the best fitting curve for the data points. Varying the ^{228}Ra activity value results in an increased or decreased $^{228}Th/^{232}Th$ maximum in Figure 2.4. This value depends on the diet and the incorporation of ^{228}Ra of the respective animal and thus could be differing for each animal. Nevertheless, a measured ratio of one indicates an ivory sample, which is at least 40 years old, whereas a ratio higher than one would indicate an ivory sample younger than 40 years. Combining the results from the ^{14}C, ^{90}Sr and the $^{228}Th/^{232}Th$ determination [9], a reliable and unambiguous age determination of ivory samples of all ages is possible.

2.3 Nuclear detection method: α-spectrometry

2.3.1 Fundamentals and detection principles

As discussed in chapter 2.1.2, a radioactive decay is accompanied by ionizing radiation. The interaction of these rays with a detector material and the resulting signal response is the base of every radiation detector. There are direct detection techniques, such as gas-flow counters and semiconductor detectors and there are indirect detection techniques, where flashes are used as signal transducer, such as the various types of scintillation detectors. Various detector set-ups are known differing in the application possibility for the type of radiation and the performance concerning operation modes, energy resolution, detection efficiency and dead time. The most common techniques for α-spectrometry are discussed in this chapter with special emphasis on the used α-spectrometry technique in this work, namely the semiconductor detection principle.

<u>Gas-flow counter</u>

Gas-flow counters are used for the detection of β- and α-radiation. Dependent on the design and operating voltage, the gas-flow counting tube works as ionization chamber [41], proportional counter [42] or Geiger-Mueller counting tube [43]. The functionality changes in this order with increased operation voltage. The proportional gas-flow counter was used in this project and is further described. The proportional gas flow counter requires a specialized counting gas, which is a neutral gas or a gas mixture like argon and methane (90:10). The radiation of the measured sample generates electrons within the counting gas, which are migrating due to an applied electric field causing further ionization of the gas during this process [44]. This significantly amplifies the effect of the initial ionization and thus generates a well evaluable current signal. This enables the determination of low-level activities and the measurement of environmental samples with a natural low activity. The differentiation of α- and β-radiation can be achieved by varying the strength of the electric field by changing the operation voltage. Typical voltages for an α-measurement and a β-measurement are 750 V and 1700 V, respectively. Since this procedure solely counts the charges created by the radiation within the measured sample and has a low energy resolution, the technique was only used for the determination of the overall β-activity of ^{90}Sr. The activity of a specific radionuclide can only be determined due to a prior specific sample preparation, which ensures that only a certain isotope (^{90}Sr) is present.

Semiconductor detectors

The semiconductor detectors are suitable for γ- and α-radiation, although the huge differences of both radiation types require and enable different construction forms of the detector. In both cases the signal transducer is a semiconductor crystal. In case of γ-radiation a high purity germanium detector is used [45]. This detector set-up requires a continuous cooling system [46] with liquid nitrogen. This is not essential in the case of a semiconductor detector for α-spectrometry, which consists of a silicon crystal [47]. The used semiconductor format in this project was the ion implanted silicon semiconductor detector [48]. Ion implantation is a method of introducing doping impurities onto the surface of semiconductors [49]. Other semiconductor detector configurations are commonly used as well, such as the diffused junction detectors [50] and the surface barrier detectors [51]. These configurations are all doped semiconductors, which aim to change the properties of the conduction or the valence band and have a huge influence on the semiconductor functionality. The ion implantation method is a very mild technique to dope surfaces [52]. The surface is exposed to a beam of the respective ions produced by an accelerator. Both the exposed area on the semiconductor surface as well as the concentration of the added impurity can be well controlled. An annealing step is carried out after the exposition, which requires a temperature of 500°C [53]. This is a far lower temperature compared to the annealing steps of other semiconductor production types, such as the diffused junction semiconductor production. Due to the mild production process, the ion implanted semiconductors tend to be more stable against ambient conditions and show an increased lifetime.

Doped semiconductors are widely used for radiation detection purposes since 1960 [53]. The radiation source produces electron-hole pairs within the semiconductor material along the path of the radiation [54]. The number of produced pairs is proportional to the energy of the α-particles. These pairs are the basic information carriers. The electron-hole pairs move in the crystal due to an applied electrical field and a signal in form of a current can be measured. A multichannel buffer assigns every measured decay, depending on its energy, to a channel number (0 – 1023). A pulse-height spectrum is recorded. By performing an energy calibration prior to the measurements (Chapter 3.3), each peak can be assigned to the respective energy and to the corresponding α-emitter.

A vacuum is applied in the detector chamber to prevent collisions of α-particles with air molecules. The sample supplement should be positioned as near to the detector as possible to maximize the counting efficiency. Unfortunately, the position of the supplement in the α-chamber has a huge impact on the α-peak shape. The energy resolution decreases with decreasing distance of sample and detector, since the full width at half maximum increases. A compromise needs to be found here for a sufficient counting efficiency and a well evaluable α-spectrum. The nature of the α-radiation enables a compact and small design compared to the space demanding high purity germanium detectors for γ-radiation measurements. The active surface of the semiconductor for α-measurement is just a few square centimeters. There is no need for an extensive shielding from exterior radiation sources, since α-particles can be blocked easily. The commercially available α-spectrometry systems contain eight so called octête chambers. Eight parallel independent measurements can be made at once in a small space. The set-up of the used α-spectrometry system is shown in Figure 2.5.

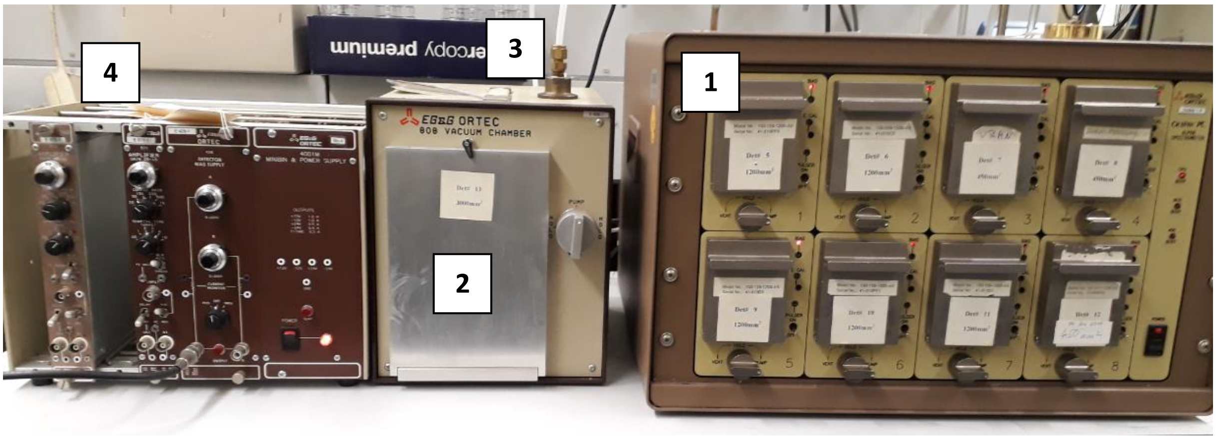

Figure 2.5: Set-up for α-spectrometry measurements. 1: Octête chambers with 450 / 1200 mm^2 active detector surfaces, 2: α-chamber with 3000 mm^2 active detector surface, 3: vacuum drain, 4: electronics.

The α-chamber systems (1 and 2) are connected to a vacuum pump (3) and to the electronic controllers (4). The controllers regulate the operation power for the semiconductor detector and read the current signal. An amplifier for signal enhancement is included and a computer for spectra display is connected. Each chamber works independently. Vacuum can be applied in one chamber independently of the pressure status of the other chambers and the electronic works flexible as well. There are also configurations, where two chambers are connected by a mutual vacuum and electronic controller. However, the set-up in Figure 2.5 enables full flexibility and a high throughput, compared to a γ-spectrometer with only one measurement possible at once.

The disadvantage of the α-spectrometry is not the measurement itself, but the extensive and time-consuming sample preparation. The α-radiation has high decay energies, such as 4.038 MeV for ^{232}Th [26], which means a high ionization potential and a good detectability via semiconductor detectors. But there are strong interactions with all molecules between the decaying radionuclide and the semiconductor. This is the reason for a mandatory vacuum in the chamber and the short distance between detector and sample. Moreover, the α-emitter hast to be electrodeposited on a steel chip for best measurement results. This technique is described in the next chapter.

2.3.2 Electrodeposition of thorium on a steel chip

In contrast to γ-spectrometry, which requires no pretreatment of the sample, the α-spectrometry requires a special supplement for best measurement results. The sample matrix shields the α-particles and significantly decreases the measurable impacts on the detector surface. Thus, the matrix needs to be removed via a quantitative and selective sample preparation. Some techniques for sample preparation are summarized in chapter 2.5. Moreover, a supplement for measurement must be created from the extracted and purified radionuclides, which has a maximum surface, minimized volume and minimized weight. This is achieved by spreading the radionuclides to a thin layer onto a contamination free surface. By doing so, a geometry standard for all samples is set and similar measurement conditions can be assumed for all measurements. The process to create a supplement for α-spectrometry is described exemplarily for thorium.

The used technique is the electrochemical deposition of thorium on a steel chip [55]. This method guarantees the controlled transfer of metal ions in a liquid phase onto the surface of a steel chip. The matrix removal needs to be complete and the separation of unwanted α-emitting nuclides needs to be done as well prior to the electrodeposition. The electrodeposition of thorium is done via the sulfate method developed by Kluge [56]. The solid residue after matrix removal is treated with concentrated nitric acid and is heated to remove organic residues from the solid phase extraction procedures. These residues would increase the layer thickness of the α-supplement with the consequence that the α-measurement would show decreased signals due to self-absorption. Since nitric acid traces would disturb the electrodeposition, hydrogen peroxide is added to remove nitric acid traces. The residue is dried under heat and dissolved in 300 µL concentrated H_2SO_4. A volume of 10 mL water is added, and the pH value is adjusted to 2.5 with ammonia solution. The solution is transferred to a self-made electrolysis cell consisting of a liquid scintillation counting Polyvial®. The bottom of the cell is a stainless-steel chip, which serves as cathode as well as substrate for the electrodeposition process. The anode is a platinum wire connected to a common laboratory power supply. The electrodeposition station used in this project is shown in Figure 2.6.

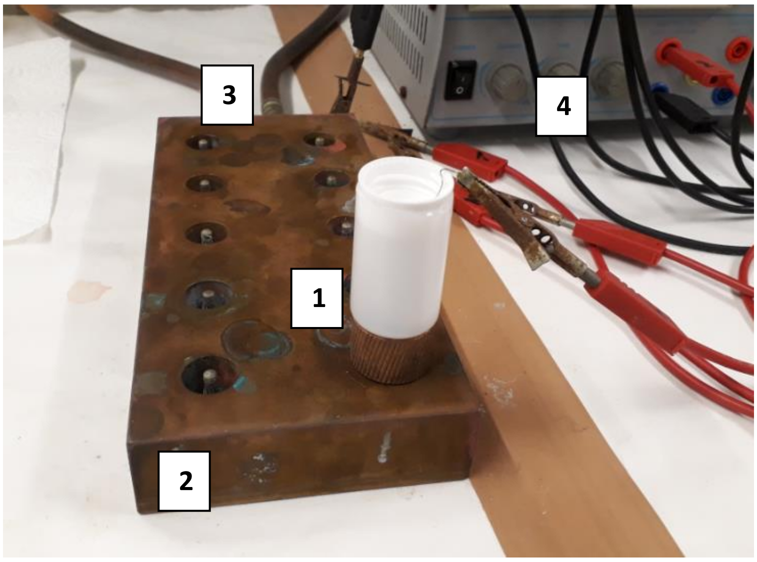

Figure 2.6: Set-up of the electrodeposition procedure. 1: electrolysis cell, 2: metal socket with slots for ten electrolysis cells, 3: water cooling, 4: power supply.

The cell is positioned in a metal socket with slots for ten cells. The metal block is hollowed to enable a water cooling of the electrochemical reaction. The electrochemical cell is described in more detail in chapter 3. The cathodic electrochemical reaction (constant 0.5 A for two hours) produces hydroxide ions from water hydrolysis (Equation 7), hence a deposition of thorium hydroxide takes place onto the steel chip surface (Equation 8).

Cathode:

$$2\,H_2O + 2\,e^- \rightarrow H_2 + 2\,OH^- \tag{7}$$

$$Th^{4+} + 4\,OH^- \rightarrow Th(OH)_4 \downarrow \tag{8}$$

Shortly before the power is switched of, 1 mL of concentrated ammonia is added [57] to complete the fixation of the thorium hydroxide on the surface. The liquid phase is removed and the steel plate is rinsed with water and acetone and dried in a nitrogen stream. A successful electrodeposition with a good suitability for measurement shows a very thin layer and no visible impurities or matrix remains. Figure 2.7 depicts a measurement supplement with a promising quality (left) and a supplement with incomplete matrix removal (right).

Figure 2.7: Steel substrates (Ø = 2 cm) after electrodeposition of thorium extracted from ivory. Left: successful matrix removal. Right: incomplete matrix removal.

The electrodeposition result on the left side is well suited for a consecutive measurement. The layer is thin, smooth and without matrix residues. The supplement on the right side shows an increased layer thickness and salt residues due to an incomplete sample preparation. The measurement of this supplement would show poor signal intensities and peak broadening. The layer needs to be removed from the chip and an additional sample preparation must be done prior to a repeated electrodeposition.

The left steel chip (Figure 2.7) is ready for measurement. The measurement time for thorium supplements made from ivory is roughly 500,000 s. Larger divergences from this value are remarked particularly during this work.

The compulsory geometry for α-spectrometry sets the electrodeposition as standard for the supplement creation for α-spectrometry. Different electrochemical cell types, which are often self-constructed are described in the literature. Teflon [58], glass [59] and plastic cells [60] are used with comparable suitability and efficiency. Various parameters, such as reaction time, buffer composition and pH value, were studied [58]. It was found that a reaction time of two hours is sufficient for an almost quantitative electrodeposition of thorium. Different substrates beside stainless steel chips are known. The huge diversity of electrodeposition substrates for α-spectrometry is shown in Table 2.4.

Table 2.4: Overview of commonly used substrates for electrodeposition of radionuclides for α-spectrometry.

Substrate material	**Application**	**Reference**
Stainless steel	Actinides	[56]
Copper	Cross-section measurement and accelerator bombardment	[61]
Carbon	Pu, U	[62]
Titanium	Pu, U	[62]
Beryllium	Heavy metal studies, lanthanides, actinides	[63]
Tantalum	Chloride	[64]
Polymer films	Extraction of Pu and U directly on polymer substrate	[65]

Although the possible selection of proper substrates is high, the substrate of choice for this project were stainless steel chips. They were cheap, disposable, could be house-made and they worked reliable with a reproducible performance. An electrodeposition of thorium suitable for an efficient measurement could be guaranteed. Several techniques for creating a supplement for α-spectrometry, besides electrodeposition, are described in the literature. Techniques with comparable results, such as slurry spreading, direct evaporation and tetraethylene glycol spreading, are known [59].

2.3.3 Evaluation of α-spectra

The evaluation of an α-spectrum results in the consecutive determination of the counts of an α-emitter, its counting rate, its activity and finally its activity concentration in a sample. The used techniques and equations are described in this chapter. The α-spectrometry measures the particle energy emitted by a radionuclide and the associated numbers of decays. The identification of α-peaks in an α-spectrum is done by comparing the measured energies to energy tables in the literature [39]. Figure 2.8 shows a typical α-spectrum deriving from thorium, which was extracted from ivory. The spectrum contains the relevant isotopes for the age determination of ivory.

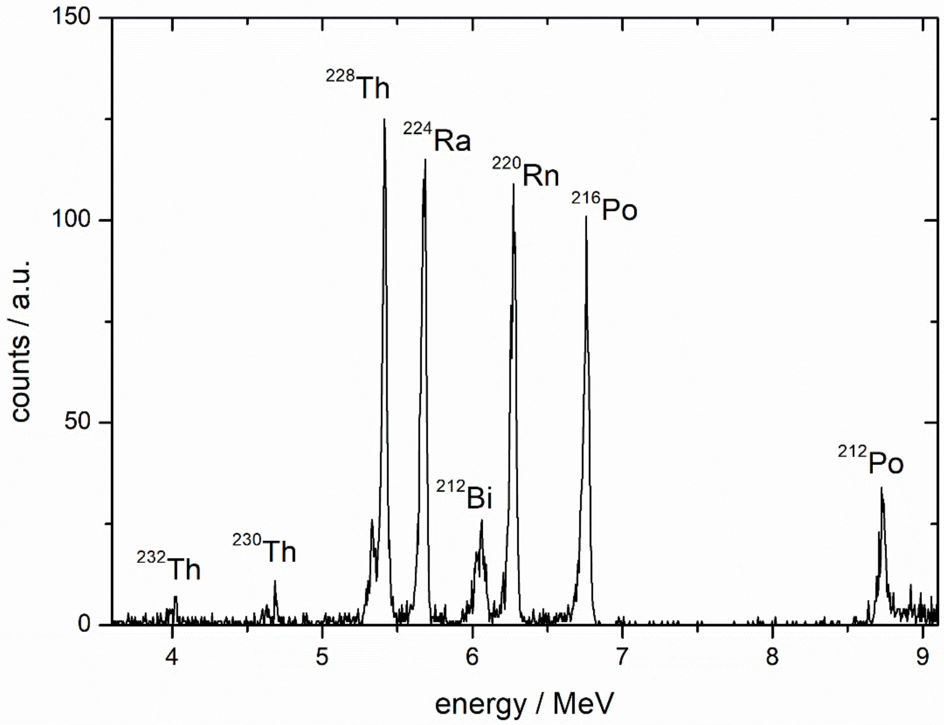

Figure 2.8: Example for an α-spectrum of thorium extracted from ivory.

Besides the thorium α-peaks, there are peaks visible with energies larger than 5.5 MeV. These are signals deriving from the decay products of ^{228}Th. These are normally not evaluated except in chapter 4.4. In some cases, there are more signals for one isotope, since an isotope can have more decay energies with different decay possibilities. Table 2.5 gives the decay properties for ^{227}Th, ^{228}Th, ^{229}Th, ^{230}Th and ^{232}Th.

Table 2.5: Decay properties of the thorium isotopes ^{227}Th, ^{228}Th, ^{229}Th, ^{230}Th and ^{232}Th. Decay properties according to [39]. Decays with an emission probability under 5% are not listed.

Thorium isotope	Energy / MeV	Emission probability / %
^{227}Th	6.038	24.2
	5.978	23.5
	5.757	20.4
	5.709	8.3
^{228}Th	5.423	73.4
	5.340	26.6
^{229}Th	5.051	6.6
	4.968	7.0
	4.902	10.6
	4.846	58.2
	4.815	9.6
^{230}Th	4.688	76.3
	4.621	23.4
^{232}Th	4.083	77.0
	3.950	23.0

The base for the activity determination of an isotope is the determination of the counts of the α-peak. First, a region of interest (ROI) needs to be defined. The ROI set the channels (C), and thus the energy range, whose counts are summed up for one decay. The full width at half maximum (FWHM) is used for this purpose. The lower bound (C_{lb}) and upper bound (C_{ub}) are defined according to Equation 9 and 10, respectively.

$$C_{lb} = C_{i,max} - 2 \cdot FWHM \tag{9}$$

$$C_{ub} = C_{i,max} + FWHM \tag{10}$$

$C_{i,\,max}$ is the channel, which shows the highest counts for the decay of an isotope i. A value of seven was chosen for the FWHM. All counts for the channels in the ROI are summed up and the activity (A) of the isotope i is calculated according to Equation 11.

$$A_i = \frac{N_i' - N_{i,0}}{t_L \cdot \eta_{phys} \cdot \eta_{ch} \cdot Y_i} \tag{11}$$

N' is the sum of all counts over the ROI, t_L is the life time of the measurement, η_{phys} is the counting efficiency, η_{ch} is the chemical yield and Y is the emission probability of the evaluated decay(s). N_0 is the value of the background counts over the ROI. The calculation of N_0 is further described in chapter 3.3. The mass of the isotope can be calculated via the activity. Equation 12 shows the relation between mass (m) and activity.

$$m = \frac{T_{1/2} \cdot M \cdot A}{ln2 \cdot h \cdot N_A} \tag{12}$$

M is the molar mass, h is the occurrence of the isotope in relation of the total element occurrence and N_A is the Avogadro constant. The chemical yield in Equation 11 represents the loss of the activity of the measured isotope during the sample preparation. The chemical yield is determined routinely via the isotope dilution analysis [66]. A yield tracer is added to the sample prior to the sample preparation. The yield tracers used in this project were ^{227}Th and ^{229}Th. The tracer is added with known activity to the sample and underlies several restrictions. The tracer must not be present in the sample itself and it must have similar chemical properties as the analyte. Since ^{227}Th and ^{229}Th are artificial thorium isotopes, which are not present in the environment, they were the first choice for the isotope dilution analysis. It is assumed that the tracer undergoes the same losses during sample preparation as the analyte. A known amount of activity of the tracer is added to the sample at the beginning of the sample preparation and measured combined with ^{232}Th and ^{228}Th in one α-measurement. The activity of radionuclide i (Equation 13) can be determined via the added activity of the tracer A_{Tr}, the emission probability of the tracer Y_{Tr} and the measured counts of radionuclide i and the tracer (N_{Tr}).

$$A_i = \frac{Y_{Tr} \cdot N_i}{Y_i \cdot N_{Tr}} \cdot A_{Tr} \tag{13}$$

2.4 Inductively coupled plasma mass spectrometry

2.4.1 Fundamentals of inductively coupled plasma mass spectrometry

Mass spectrometry (MS) is a versatile and universal detection method for atoms and molecules. The determined value is the mass to charge (m/z) ratio of the analytes. The base for the development of the MS was set around the turn of the century. Dempster [67] developed and built the first modern mass spectrometer in 1918. This was the base for several modifications and applications for MS, which followed during the 20th century. The function principle is the separation of charged atoms or molecules in an electromagnetic field with a consecutive detection. The composition of a MS set-up can be divided into an ionization source, an analyzer and a detector.

The ionization source produces gas phase ions from all compounds in the sample. This can be done via various ionization source types. There are hard ionization techniques, such as electron ionization [68] and inductively coupled plasma ionization [69]. The electron ionization results in a high degree of fragmentation of the analyzed molecules. This provides an increased amount of information used for structure analysis. Inductively coupled plasma ionization is a widely used technique for elemental analysis of cations using an argon plasma. It completely cleaves all molecular bonds. Since this ionization technique is the used technique in this project, the technique is described in more detail during this chapter. Soft ionization techniques are used, when the structure of the analyzed molecules should be preserved for detection. Examples for soft ionization are electrospray ionization [70], atmospheric-pressure chemical ionization [71] and matrix-assisted laser desorption ionization [72]. Each ionization technique has its advantages and suitability for different applications.

The analyzer separates the gas phase ions, produced by the ionization technique, in an electric or magnetic field. The ions are separated due to their (m/z) ratio. The most common mass analyzers are the sector field instruments [73], the time-of-flight analyzers [74] and the quadrupole mass filters [75]. A sector field mass analyzer separates the charged ions in an electrical field and, in case of a double focused version, a subsequent magnetic field. Ions with lower mass are more affected by the deflection as ions with higher mass. This discrimination enables the differentiation of ions by the mass. The time-of-flight mass analyzer determines the mass of the analytes via the flight time between ionization and detection. Therefore, the ions are accelerated by the same potential and they are moving through a vacuumed chamber and reach the detector. The velocity of the ions depends on the (m/z) ratio, whereas ions with lower mass move faster as ions with higher mass. The quadrupole mass filter consists of four parallel rod electrodes with applied oscillating electrical fields. This electric field stabilizes and destabilizes ions according to their (m/z) ratio. Only ions with a certain (m/z) ratio pass the quadrupole and are counted by the detector. The ions, which can pass the quadrupole, are selected by a rapid change of the electric field.

The third part of a mass spectrometer is the detector. Typically, an electron multiplier [76] or a Faraday cup [77] is used. The detector counts the ions, which pass the mass analyzer. In combination with the (m/z) ratio data from the mass analyzer, a mass spectrum can be recorded.

A specialized set-up for MS should be mentioned here, since it is widely used for the analysis of radionuclides. The accelerator mass spectrometry [4] works with two mass spectrometers and a particle accelerator. Negative charged ions are generated by a sputter ion source and pass a mass analyzer for a first mass selection prior to the acceleration. The subsequent acceleration via millions of volts and the passing through thin matter shifts the charge of the particles from negative to positive. A last mass analyzer stage enables the detection of nuclides with high interference suppression. Thus, the precise analysis of rare isotopes, such as ^{14}C, with very low background is possible [13].

The used technique for MS in this project is the inductively coupled plasma mass spectrometry (ICP-MS). Figure 2.9 shows the overall set-up of the used ICP-MS instrument.

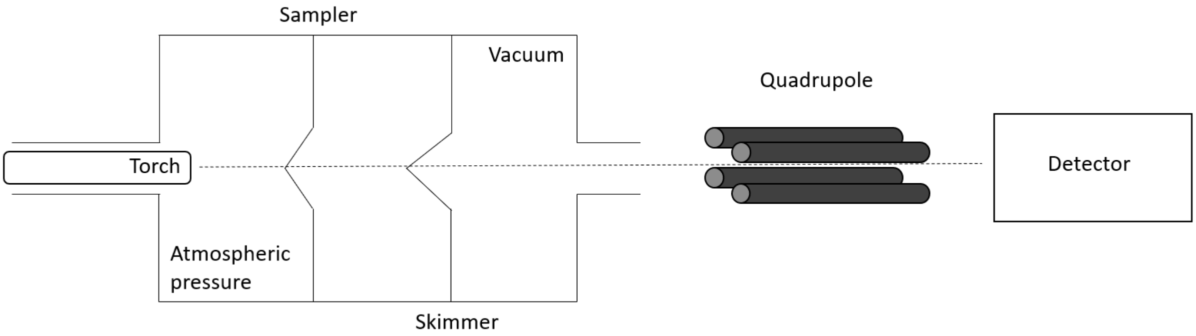

Figure 2.9: Scheme of the used ICP-MS set-up.

The set-up consists of an injection system (pump, nebulizer, spray chamber and torch), the interface region (sampler and skimmer cones and the transition to the vacuum) and the mass spectrometer. The analyte passes the instrument in this order. The sample introduction system, including the plasma torch, is described in more detail in Figure 2.10 and Figure 2.11.

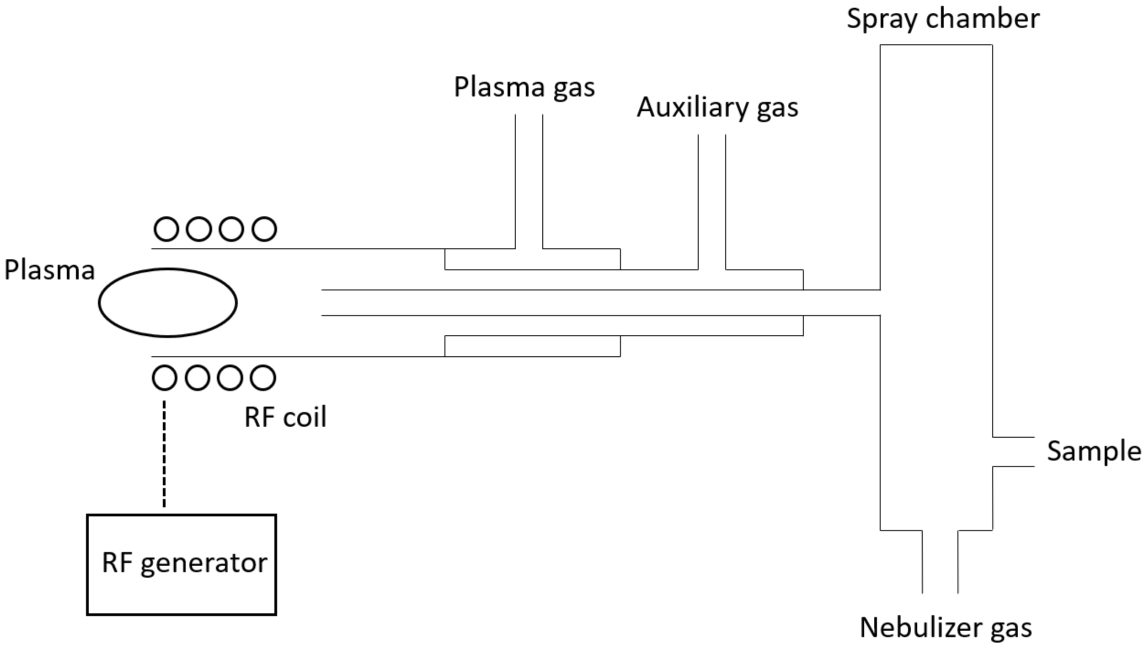

Figure 2.10: Schematic depiction of the injection system of the ICP-MS. RF = radio frequency.

Figure 2.11: Photo of the plasma torch.

Three argon gas supplies are necessary for an ICP-MS set-up. The plasma is generated and constantly supplied by the argon plasma gas stream at the end of the quartz torch. The radio frequency copper coil and an induced electric spark ignite the plasma and the radio frequency, generated by the RF generator, sustains the plasma during the operation time. The argon auxiliary gas stream cools the plasma and shields the glass torch from the plasma. The plasma reaches temperatures up to 10,000 K. The argon nebulizer gas feeds the sample through the spray chamber into the torch. The sample is delivered at a 90° angle towards the nebulizer gas. An aerosol is formed in the spray chamber and the collisions with the surfaces produce fine droplets, which are fed into the torch at a 90° angle. The sample enters the plasma and all compounds in the sample are ionized and all molecular bindings are cleaved. The sample beam, consisting of ionized sample and plasma, passes the interface region. Two cones with inlet hole diameters of one millimeter (Figure 2.12) reduce the sample beam flow to prevent an overloading of the mass spectrometer and the detector. While atmospheric pressure is present in the torch region, the first vacuum stage is between the sampler and the skimmer cone.

Figure 2.12: Left: sampler cone, right: skimmer cone.

The next stage after the interface region and the focusing due to the cones and the ion optics is the quadrupole mass analyzer, which separates the ionized atoms in the sample due to their (m/z) ratio. An electron multiplier detects the ions. The shown set-up of ICP-MS is the basic version and can be upgraded to improve the instrument performance. Reaction and collision cells can be included in the set-up. The dynamic reaction cell is located before the quadrupole analyzer and can be filled with a reaction gas [78]. This gas reacts with interferences and improves the sensitivity of the instrument.

The hard ionization of the hot plasma disables the possibility of the ICP-MS to do molecule analysis. All bindings within the molecules are cleaved and just positively charged ions are formed during the ionization process. The strength of the ICP-MS is the elemental analysis and various applications for trace metal analysis are known. The application variety is described in more detail within the next chapter. The sensitivity of ICP-MS is very high, and the limit of quantification is within the range of 4 ng per L and 4 µg per L [79]. The limit of detection and quantification depend on the analyzed element and all interferences, caused by the sample matrix. Two main interferences are contributing to a decreased sensitivity of the measurement. Isobaric interferences are caused by isotopes, which have the same (m/z) ratio as the target analyte. The titanium isotope with the highest abundance ^{48}Ti is interfered by the calcium isotope ^{48}Ca. The isobaric interferences depend on the isotope content in the sample and can be prevented by a previous extraction of the target analyte from the sample matrix. Polyatomic interferences are caused due to the high temperatures and the potential reactivity of all atoms in the argon plasma. All atoms, which are always present in the plasma ($^{36/38/40}Ar$, $^{17/18/19}O$, $^{12/13}C$ and $^{14/15}N$), can react with the sample or each other and form polyatomic compounds. These compounds can have similar masses as the target analyte and simulate an increased concentration of the analyte (e.g. $^{40}Ar^{14}N^{1}H$ interferes with ^{55}Mn [80]).

The quantification of metals by ICP-MS demands the technique of the internal standard. Each element has a different sensitivity for the used ICP-MS set-up and analyte losses during the sample injection or discrimination effects must be compensated to determine the correct analyte concentration. The use of an internal standard is recommended. After the sample preparation and prior to the measurement, the internal standard is added to all solutions, which are measured. The internal standard is added to the calibration solutions and to the sample solutions with the same concentration. It is assumed that the internal standard undergoes similar losses and discriminations during measurement as the analyte. Since the added concentration of the internal standard is known, the concentration of the analyte x (c_x) is calculated according to Equation 14.

$$\frac{i_X}{i_{IS}} = m \cdot \frac{c_X}{c_{IS}} + b \tag{14}$$

I_X and i_{IS} are the background corrected measured intensities of the analyte x and the internal standard (IS). C_{IS} is the known concentration of the internal standard. M is the slope of the calibration curve and b is the y-intercept of the calibration curve. Since the ICP-MS is a mass sensitive measurement technique, the internal standard should have a mass similar to the mass of the analyte. The ICP-MS measurements for ^{232}Th were conducted with ^{209}Bi as internal standard, because ^{209}Bi is the heaviest metal, which fulfills all requirements for this measurement situation. It is not present in the sample, it has a high mass and it shows no interferences in a subsequent α-measurement.

2.4.2 Application of ICP-MS for radionuclide detection

The application field of ICP-MS, as described in the previous chapter, is mainly the elemental analysis. All kind of samples can be analyzed with or without prior sample preparation. The spectrum of elemental analysis is broad. Sulfur in organic samples [81], transition metals in sea water [82] or titanium in blood serum [83] are a few examples for the various applications of ICP-MS. Although the ICP-MS is not suitable to analyze whole molecules, it is used to determine the total metal content in biomolecules, such as proteins [84]. The extraordinary functionality for trace metal analysis enables the application of ICP-MS as a coupled detection technique for various separation techniques. High-performance liquid chromatography is often used as separation technique with a coupled ICP-MS as detection technique [85]. The electro migrative separation technique capillary electrophoresis can be coupled to ICP-MS as well [86].

An application field for ICP-MS is the determination of long-lived radionuclides. Many radionuclides, which are relevant for environmental analysis, are metals and therefore accessible by ICP-MS. Isotopes of the elements cobalt, iron, nickel, uranium and thorium are often analytes for the purpose of environmental monitoring. Depending on the activity of the radionuclides in the sample, the determination by the common radiation-based detection techniques, such as α-, β- and γ-spectrometry, works reliable and well. High activities can be determined with low uncertainty. For low activities, as it is the case for long-lived radionuclides in environmental samples, the radiometric approach is limited. The sensitive technique ICP-MS is used in this field to determine the concentration of radionuclides, such as ^{229}Ra, ^{230}Th, ^{237}Np, ^{238}U, ^{239}Pu and ^{241}Am [87]. Especially in the context of age dating the determination of radionuclides by ICP-MS is a useful tool. The age determination of zircon is done by U-Pb dating including the ICP-MS measurement of uranium and lead isotopes [88].

The longevity of these isotopes reduces the signal intensity in radiometric detection techniques and thus increases the uncertainty of the determination. Since the ICP-MS detection is not based on the decay process of the isotopes but on the (m/z) ratio, the ICP-MS is well suited for the analysis of long-lived isotopes with a low limit of detection. That is not the case for isotopes, which show a short half-time and lower concentration. The analytical challenge in this project represents this situation. ^{228}Th and ^{232}Th should be determined reproducible and with low uncertainty. ^{232}Th is a natural isotope, which is omnipresent in the environment and shows a rather high concentration and a half-life of $14.1 \cdot 10^9$ years [39]. ^{228}Th has a short half-life of 1.91 years [39] but marginal concentration in the environment [26]. ^{228}Th is not accessible for ICP-MS since its concentration is under the limit of detection of the ICP-MS but well it is measurable via α-spectrometry because of the high activity and low half-live. ^{232}Th however, shows low activities in α-spectrometry but sufficient signal intensity in ICP-MS measurements. It seems straight forward to use the ICP-MS as an additional detection technique for the determination of the isotope ^{232}Th in the context of ivory dating.

2.5 Radiochemical sample preparation

2.5.1 Fundamentals of radiochemical sample preparation

Radiometric detection techniques require extensive sample preparation. Dissolving the sample matrix under acidic conditions, dependent on the sample nature, is always the first step in this procedure. While this is often enough for λ-spectrometry, β-spectrometry and α-spectrometry are far more demanding for matrix removal and purification. α-radiation has high decay energies, but this radiation can easily be blocked by e.g. a sheet of paper. The self-absorption [89] of the sample itself is an issue to overcome. In case of α-spectrometry, it is necessary to create a supplement, which is suitable for an α-spectrometric measurement. This is done by spreading the extracted analyte to a thin layer (see chapter 2.3.2). This procedure minimizes the self-absorption effects and sets a geometry standard for all supplements for calibration. It is convenient to minimize matrix residues and to separate radionuclides with similar (disturbing) decay energies in advance of the measurement.

The Radiation Protection Ordinance [90] regulates the radiation protection laws in Germany and states beside other things the limits of the allowed activities in waste. Waste material, such as waste water, construction material and air filters are typical samples for the determination of nuclide vectors. Since the activity limits are low and new future regulations could lower them further, it is an analytical challenge to achieve required limit of detections and to applicate the suitable analytical sample separation procedure. In a low-level activity range, the analyte content is in a concentration range of lower than ppb. The sample preparation needs to have a high chemical yield as well as a sufficient selectivity. Furthermore, the sample preparation procedures need to work for high salt contents.

Regarding the importance of ICP-MS measurements in this project, the sample preparation gains more importance, since isotopes with similar mass as the analyte can interfere in ICP-MS measurements. The thorium isotope measured by ICP-MS is ^{232}Th, which is a highly suitable isotope for ICP-MS, since in this high mass range are no polyatomic interferences. That would not be the case for isotopes with similar mass as 232 amu, such as ^{232}U. Although the ^{232}U can easily be distinguished from ^{232}Th due to its higher α-decay energy within the α-spectrometric measurement, it would heavily falsify the ICP-MS measurement if it is present in comparable concentration as ^{232}Th. The quantitative separation of ^{232}U from ^{232}Th must be fulfilled by the sample separation. Furthermore, working with low-level activities, a sample contamination needs to be prevented. In case of the thorium determination in ivory, some traces of sand or dust, which is known to contain thorium [38] would lead to a wrong age interpretation.

All these issues need to be considered for the radioanalytical sample preparation process. There are several tailored methods for the cause of radiochemical sample preparation with a broad spectrum of modern and old-fashioned techniques. The next chapters give an overview of used techniques with increased respect for the techniques, which were applied for the thorium extraction from ivory.

2.5.2 Liquid – liquid extraction

Liquid-liquid extraction is based on the distribution of compounds between two immiscible solvents due to the differing affinity of the compounds towards the respective solvent. The system consists of a polar and a nonpolar solvent, which separates polar analytes from nonpolar matrices or vice versa. In case of a nonpolar phase, in which a specific ion can be solved, a separation of this ion from the matrix, which remains in the polar phase is possible. This technique is used for the extraction of the radionuclide ^{55}Fe. Diisopropylether is used for extraction of ^{55}Fe from various sample matrices, with a successive re-extraction with 0.05 M H_2SO_4 [91]. If simple systems cannot be found, the analyte is transferred into a form, which is accessible for a simple liquid-liquid extraction procedure. For the analysis of $^{59/63}Ni$, the nickel is treated with the complex former dimethylglyoxime. In the complexed form, it can be extracted with chloroform [92]. Another option is the addition of an extraction compound to the nonpolar phase. Trioctylphosphine oxide (TOPO) dissolved in cyclohexane can selectively extract thorium from inorganic mixtures with high salt content [93], such as ivory. The tolerance towards high salt concentrations [94] makes the liquid-liquid extraction a versatile and selective separation technique for radionuclides from all kind of matrices. Drawback of this sample preparation technique is the high liquid waste generation, which is a significant financial investment if the waste must be treated as active waste according to the Radiation Protection Ordinance. Furthermore, the technique is less suited for automatization.

2.5.3 Solid phase extraction

The disadvantages of the liquid-liquid extraction techniques can be overcome by shifting the system to a solid phase extraction procedure (SPE). A solid phase extraction system consists of a mobile phase and a stationary phase, which is a selective and solid column material. The analyte remains on the column and the matrix components are eluted without column interaction. The loaded column is washed, and the analyte is eluted using the required solution. The waste production is reduced, and the system can be easily automatized [95]. More SPE procedures can be supervised at once, which enables a high sample throughput. The diversity of column materials is high. Molecules can be imprinted into polymers for various target analytes and applications, such as nicotine [96], pesticides [97] and heavy metal ions [98]. Different SPE cartridges with different column materials can be stacked to separate one analyte after the other from the same sample digestion solution. Figure 2.13 shows the simultaneous separation of thorium, uranium and americium in one SPE procedure [99]. After the loading step, the cartridges are separated and the radionuclides are eluted individually.

Figure 2.13: Simoultaniously separation of various radionuclides in one SPE procedure.

Presumed that a suitable column material can be found, every liquid-liquid extraction system can be converted to a solid phase extraction procedure. Instead of using TOPO in cyclohexane [93] for the extraction of ^{232}Th and ^{228}Th for the purpose of age determination of ivory, the TOPO can be impregnated on Chromosorb®, which quantitatively separates thorium from matrix components in a SPE procedure. Since this procedure cannot separate actinides from each other, an additional SPE procedure must be conducted to remove disturbing actinide radionuclides from thorium isotopes. There are commercially available column materials, which show a high selectivity for actinides. The resin TEVA® shows a high uptake of tetravalent actinides in the range of 2 – 4 M nitric acid [100]. The Th^{4+} can be eluted selectively by switching to 9 M HCl, while Pu^{4+}, Np^{4+} and U^{4+} remain on the column [100]. The successive use of TOPO/Chromosorb® and TEVA® resin achieves the quantitative matrix removal and the selective extraction of the thorium isotopes from ivory.

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3. Experimental

In this section, the used materials and methods are described. Specific descriptions of the tailored chemicals and methods for the chapters 4.1, 4.2, 4.3, 4.4 and 4.5 can also be found in subsections of the respective chapters. However, in the following an overview of all used chemicals, consumables, methods, instruments and quality management is given. All used chemicals were analytical grade and used without further treatment.

3.1 Materials

Chemicals

Table 3.1. List of used chemicals.

Chemical	Supplier
Aluminum nitrate nonahydrate p.a.	Merck KGaA (Darmstadt, Germany)
Ammonium chloride p.a.	Merck KgaA (Darmstadt, Germany)
Ammonia solution 25% p.a.	VWR Chemicals (Ismaning, Germany)
Ascorbic acid p.a.	Merck KgaA (Darmstadt, Germany)
Bismuth ICP-MS standard 1 ppm	Spetec GmbH (Erding, Germany)
Calcium chloride p.a.	Carl Roth, GmbH & Co. KG (Karlsruhe, Germany)
Chromosorb® W-AW-DMCS, 80-100 mesh	CS-Chromatographie Service GmbH (Langerwehe, Germany)
Dowex® 50WX8 hydrogene form, 200-400 mesh	Sigma-Aldrich (Seelze, Germany)
Hydrochloric acid 37% p.a.	VWR Chemicals (Ismaning, Germany)
Nitric acid 65% p.a.	Merck KGaA (Darmstadt, Germany)
Sulfuric acid 95% - 97% p.a.	VWR Chemicals (Ismaning, Germany)
Nitric acid 65% ultrapure	Merck KGaA (Darmstadt, Germany)
Hydrofluoric acid 38% p.a.	VWR Chemicals (Ismaning, Germany)
Hydrogen peroxide 30% p.a.	VWR Chemicals (Ismaning, Germany)
Lactic acid 98% p.a.	Sigma-Aldrich (Seelze, Germany)
Silver nitrate p.a.	Sigma-Aldrich (Seelze, Germany)
Sodium hydroxide p.a.	Sigma-Aldrich (Seelze, Germany)

Oxysolve C-400	Zinsser Analytic GmbH (Eschborn, Germany)
Catalysator – platinum on aluminum	Sigma-Aldrich (Seelze, Germany)
Strontium nitrate p.a.	Fluka Inc. (Buchs, Switzerland)
TEVA® resin	Triskem International (Bruz, France)
Thorium ICP-MS standard 1 ppm	Spetec GmbH (Erding, Germany)
Thorium Tracer ^{227}Th 28 mBq/mL (01.03.2018)	PTB (Braunschweig und Berlin, Germany)
Thorium Tracer ^{229}Th 5 mBq/mL (01.01.1994)	PTB (Braunschweig und Berlin, Germany)
Trioctylphosphine oxide p.a.	Merck KGaA (Darmstadt, Germany)
Uranium ICP-MS standard 1 ppm	Merck KGaA (Darmstadt, Germany)
UTEVA® resin	Triskem International (Bruz, France)

Consumables

Table 3.2: List of used consumables.

Consumables	Supplier
Argon 4.6	Linde AG (Pullach, Germany)
Calcium Cell Test 100858	Merck KGaA (Darmstadt, Germany)
Centrifuge tubes SuperClear 15 mL	VWR Chemicals (Ismaning, Germany)
ISOLUTE® Frits 3 mL 20 µm PE	Biotage (Uppsala, Sweden)
ISOLUTE® Frits 6 mL 20 µm PE	Biotage (Uppsala, Sweden)
ISOLUTE® Reservoir 3 mL	Biotage (Uppsala, Sweden)
ISOLUTE® Reservoir 6 mL	Biotage (Uppsala, Sweden)
LSC Polyvials 20 mL	Zinsser Analytic GmbH (Frankfurt, Germany)
Nitrogen 5.0	Linde AG (Pullach, Germany)
NORM-JECT® syringe 20 mL	Henke Sass Wolf (Tuttlingen, Germany)
Oxygen	Linde AG (Pullach, Germany)
P-10 counting gas (90:10, argon: methane)	Linde AG (Pullach, Germany)
Rotilabo® syringe filter 0.45 µm PTFE	Carl Roth, GmbH & Co. KG (Karlsruhe, Germany)
Smart Tune Solution	PerkinElmer (Rodgau, Germany)
Steel discs Ø 2 cm	Mechanical workshop University Regensburg
Ultrapure water (resistivity > 18MΩ/cm)	Milli- Q Advantage A10 system, Merck Millipore (Darmstadt, Germany)
Various syringes	B. Braun Melsungen AG (Melsungen, Germany)

Instruments

Table 3.3: List of used instruments.

Instrument	Software	Supplier
Furnace model Thermicon T	Inaccessible	Heraeus Holding GmbH (Hanau, Germany)
Vertical tube furnace	Inaccessible	Carbolite Gero GmbH & Co. KG (Neuhausen, Germany)
Quantulus 1220 liquid scintillation counter	WinQ 1.2	PerkinElmer (Rodgau, Germany)
Berthold LB770-2 gas-flow counter	UMS 1.09p	Berthold Technologies (Bad Wildbad, Germany)
Photometer Spectroquant Nova 60	Inaccessible	Merck KGaA (Darmstadt, Germany)
ICP-MS model ELAN 9000	ELAN Software 3.0	PerkinElmer (Rodgau, Germany)
Octête α-chamber U-034-1200-AS	Gamma Vision 5.1	EG&G Ortec (Meerbusch, Germany)

Ivory samples

The used ivory samples are summarized in this chapter. They had variable origins and they were analyzed for different purposes and according to different methods. Some samples were analyzed several times. The samples are summarized in Table 3.4 and a more detailed specifications can be found in the experimental parts of the chapters 4.1, 4.2, 4.3, 4.4 and 4.5.

Table 3.4: Specifications of analyzed ivory samples. The code is a company internal label system. The numbers are assigned consecutively for each new sample.

Code	Chapter	Supplier zoo	Sample drawing	Code	Chapter	Supplier zoo	Sample drawing
193	4.1	Basel	01.07.2012	260	4.1, 4.3	Basel	08.01.2005
194	4.1	Wuppertal	15.10.2012	261	4.2, 4.3	Basel	29.07.2010
195	4.1	Wuppertal	20.05.2010	262	4.1, 4.3	Basel	11.08.2012
196	4.1	Wuppertal	19.07.2011	263	4.1, 4.3	Basel	14.02.2013
197	4.1	Wuppertal	23.01.2013	264	4.3	Basel	03.10.2013
198	4.1	Wuppertal	25.01.2013	265	4.2, 4.3	Basel	10.10.2013
199	4.1	Wuppertal	10.04.2014	266	4.1, 4.2	Basel	18.02.2016
200	4.1	Wuppertal	01.07.2014	268	4.1, 4.2	Basel	20.04.2017
201	4.1	Wuppertal	01.07.2015	269	4.1, 4.2	Basel	03.01.2018
202	4.1	Wuppertal	01.07.2010	270	4.1	Basel	09.11.1998
206	4.1	Wuppertal	03.02.2016	271	4.1	Basel	14.08.2003
207	4.1 - 4.4	Wuppertal	09.01.2016				
BfN7	4.3, 4.5	BfN*	2005				

*German Federal Agency for Nature Conservation

3.2 Methods

The extensive experimental procedure for age determination of ivory, including the isotopes ^{14}C, ^{90}Sr, ^{228}Th and ^{232}Th, is described in this chapter. The modified method with integrated ICP-MS measurements within the analytical procedure is described as well.

Incineration at 650°C

The raw ivory was cleaned from dirt and other impurities and crashed to smaller pieces (Ø 5 mm). It was positioned in a silica glass tube with a platinum catalysator and an oxygen stream was applied. The tube was heated up to 650°C by a tube furnace. The stream of oxygen and incineration products was conducted through two water-cooled bubble counters, a washing flask with bidest. water and two successive washing flasks filled with 150 mL 1 M NaOH each. The carbon content in the ivory was oxidized to CO_2 and adsorbed in the NaOH solution. The inorganic compounds of the ivory remained in the glass tube in form of ivory ash. The remaining ash was milled and treated with concentrated nitric acid to remove remaining organic traces and heated until dryness. The procedure was repeated with concentrated hydrochloric acid.

^{14}C

The pH value of the united NaOH solutions was adjusted to 11 with 5 M NH_4Cl and a volume of 25 mL of 5 M $CaCl_2$ solution was added to precipitate the $CaCO_3$. The $CaCO_3$ was filtered and dried over night at 100°C. The precipitate was dispersed in 10 mL water in a three-necked flask and treated with 95 mL 2 M HCl. The released CO_2 was conducted through a $AgNO_3$ trap and a drying tube filled with $CaCl_2$ with a nitrogen gas stream. Subsequently, the CO_2 was directly adsorbed in 20 mL Oxysolve C-400, which was water-cooled and stirred. The measurement of the ^{14}C activity was done after at least five days with a liquid scintillation counter for 2000 minutes.

^{90}Sr

The calcium content of the ivory ash was determined via a photometric cell test kit. An amount of ivory ash, which did not exceed 2.5 g of calcium, was dissolved in 6 M HCl and 1.5 M lactic acid (1:1). 50 mg of strontium and a thorium yield tracer (^{227}Th or ^{229}Th; 30 mBq) were added. The compounds of the ivory ash were separated using a hot (87°C) ion chromatography procedure. The column was laboratory-constructed and could be heated up by a water circulation system jacketing the column material. The column procedure and the separation parameters are described in Table 3.5. The eluate fraction containing strontium was treated with 60 mL concentrated H_2SO_4 and the precipitate was filtered and measured after two weeks with a gas-flow counter for 2000 minutes.

Table 3.5: Procedure and parameters of the column-based sample preparation steps. The used extraction reagents were Dowex, Trioctylphosphine oxide (TOPO) and TEVA® resin.

	Hot ion chromatography	**TOPO SPE**	**TEVA® SPE**
Column material	Dowex® 50WX8 (151,6 g with Ø 4 cm)	TOPO on Chromosorb® (1 cm with Ø 1.2 cm)	TEVA® resin (150 mg)
Conditioning	250 mL 1.5 M lactic acid	10 mL 1 M HNO_3	10 mL 3 M HNO_3
Analyte elution	800 g 1.5 M Ammonium lactate (pH = 7) 210 g - 340 g: Th-fraction 480 g - 800 g: Sr-fraction	10 mL 0.1 M H_2SO_4	2 mL 9 M HCl
Flow rate	2.5 mL / min	1 mL / min	1 mL / min
Reconditioning	600 mL 6 M HCl	-	-
Reusable	yes	no	no

^{232}Th and ^{228}Th

The thorium fraction deriving from the hot ion chromatography procedure was heated and the solvent volume was reduced to 10 mL. A volume of 100 mL of 3 M HNO_3 / 1 M $Al(NO_3)_3$ solution was added and two consecutive solid phase extraction (SPE) procedures were conducted. In case of a solely thorium analysis without the need of ^{14}C and ^{90}Sr, such as it is the case in chapter 4.2, 4.3, 4.4 and 4.5, the experimental procedure was shortened. The raw ivory was incinerated at 650°C in a muffle furnace without an oxygen stream. The ash was dissolved in 3 M HNO_3 / 1 M $Al(NO_3)_3$ and the thorium tracer was added. The SPE procedures followed directly without the need of the hot ion chromatography. The SPE protocols can be found in Table 3.5. The first column material was trioctylphosphine oxide impregnated on Chromosorb® W-AW-DMCS. 4 g $Al(NO_3)_3$ and 150 mg ascorbic acid were added to the eluate. The second column material was TEVA® resin. The eluate was fumed down to dryness and treated with hydrogen peroxide until the solid residue was white. The α-spectrometry required a special measurement geometry, where the thorium was spread as a thin layer on a smooth surface. This was done by electrodeposition (see chapter 2.3.2) of the eluate residue on a steel chip. Therefore, the residue was dissolved in 300 µL conc. H_2SO_4, a volume of 10 mL water was added and the pH was adjusted to 2.5 using ammonia. The solution was transferred to the house-made electrochemical cell (Figure 3.1). The electrodeposition was done by constantly applying 0.5 A over a period of two hours. The supplement was measured in an α-chamber for five days.

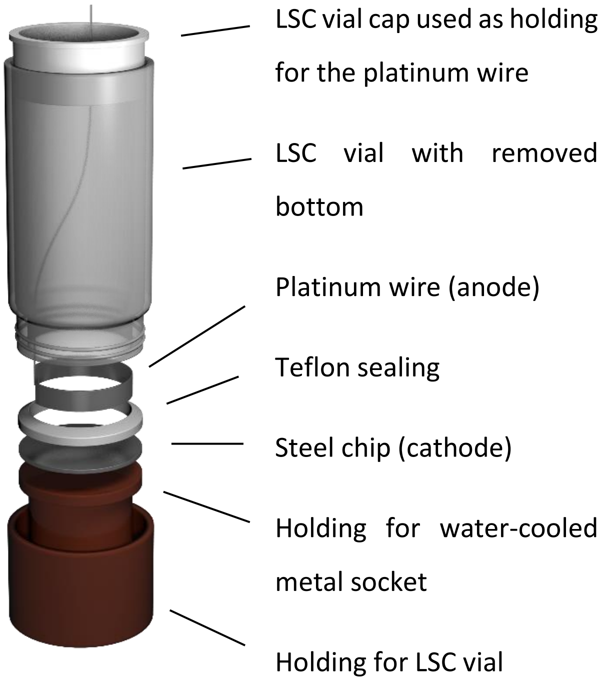

Figure 3.1: Schematic depiction of the house-made electrochemical cell.

^{232}Th with ICP-MS

An ICP-MS analysis for ^{232}Th was integrated in the experimental procedure in chapter 4.3 and 4.5. That was done as described in the following. The eluate deriving from the TEVA® column was heated to dryness. The residue was dissolved in 1% HNO_3. The internal standard ^{209}Bi was added and the volume was set to 10 mL with 1% HNO_3. The measurement was done using an external calibration in the range of 0.5 ppb – 10 ppb. All solutions were filtered using a 0.45 µm syringe filter. After the measurement, the remaining sample solution was heated until dryness and the procedure of electrodeposition for the α-spectrometric measurement proceeded as described above.

3.3 Quality management

The most important analytical instruments used in this work, namely α-spectrometer and ICP-MS, were routinely checked and serviced. A performance record was done per working day as well as a performance check over the whole duration of this dissertation project. This chapter describes the processed actions, which guaranteed the functionality of the instruments and a high quality and reliability of the measurements.

α – spectrometry

Background

Since the background of an α-spectrometric detection chamber should be as low as possible [1] to enable low-level [2] alpha decay detection the long-term background stability was observed. This was done by queuing background measurements between measurements of thorium supplements. The α-chambers used in this project were reserved for the measurement of thorium supplements to prevent contamination with other radionuclides. The α-chambers were labeled with chamber No. 2, 6, 7 and 8. The background observation of chamber No. 8 was chosen as a basis for discussion in this chapter. The mean background counting rate was calculated by evaluating background measurements of several years to assume a representative value of the expected background for the upcoming measurement. Figure 3.2 shows the background of the ^{232}Th energy range in form of the background counting rate (R_0).

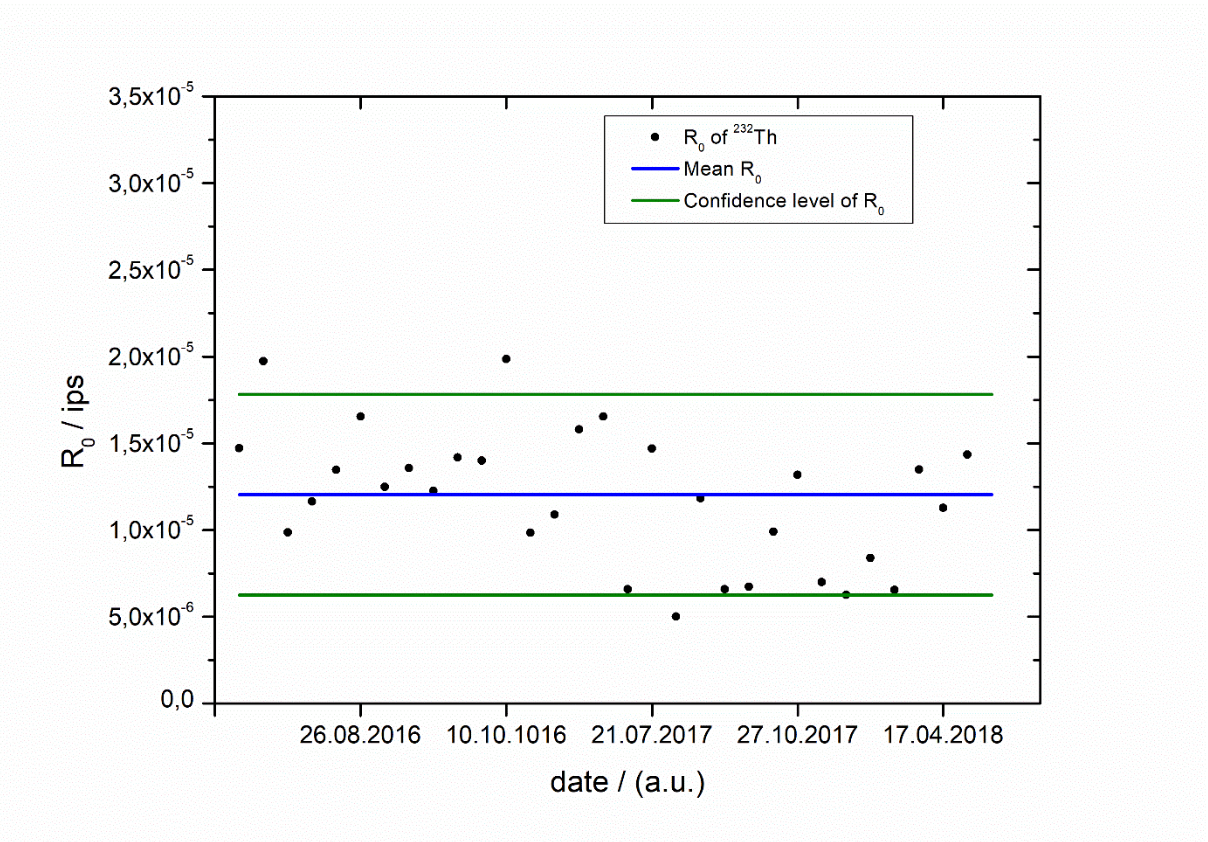

Figure 3.2: Observation of the background counting rate (R$_0$) of the energy range of ^{232}Th in α-chamber No. 8. Confidence level of 95%.

The measured R$_0$ values scattered around the mean value of $1.2 \cdot 10^{-5}$ ips and were stable over the last three years without larger spikes. Compared to a typical counting rate for thorium supplements made from ivory, R$_0$ contributed to the overall measured counting rate for the ^{232}Th energy range with roughly 20%. Thus, the background counting rates contributed heavily to the calculated uncertainty of the thorium activity determination, which made the background observation even more necessary to prevent increased background counting rates due to contaminations in the chamber. Figure 3.3 depicts the situation of the background in the energy range of ^{228}Th. A similar observation as in Figure 3.2 could be made, with exception of a different mean value of R$_0$ of $2.1 \cdot 10^{-5}$ ips. In three cases (e.g. measurement on 26.08.2016), Figure 3.3 shows a significant exceeding of the mean value of R$_0$. This was caused by a previous measurement of a higher active thorium supplement in chamber 8.

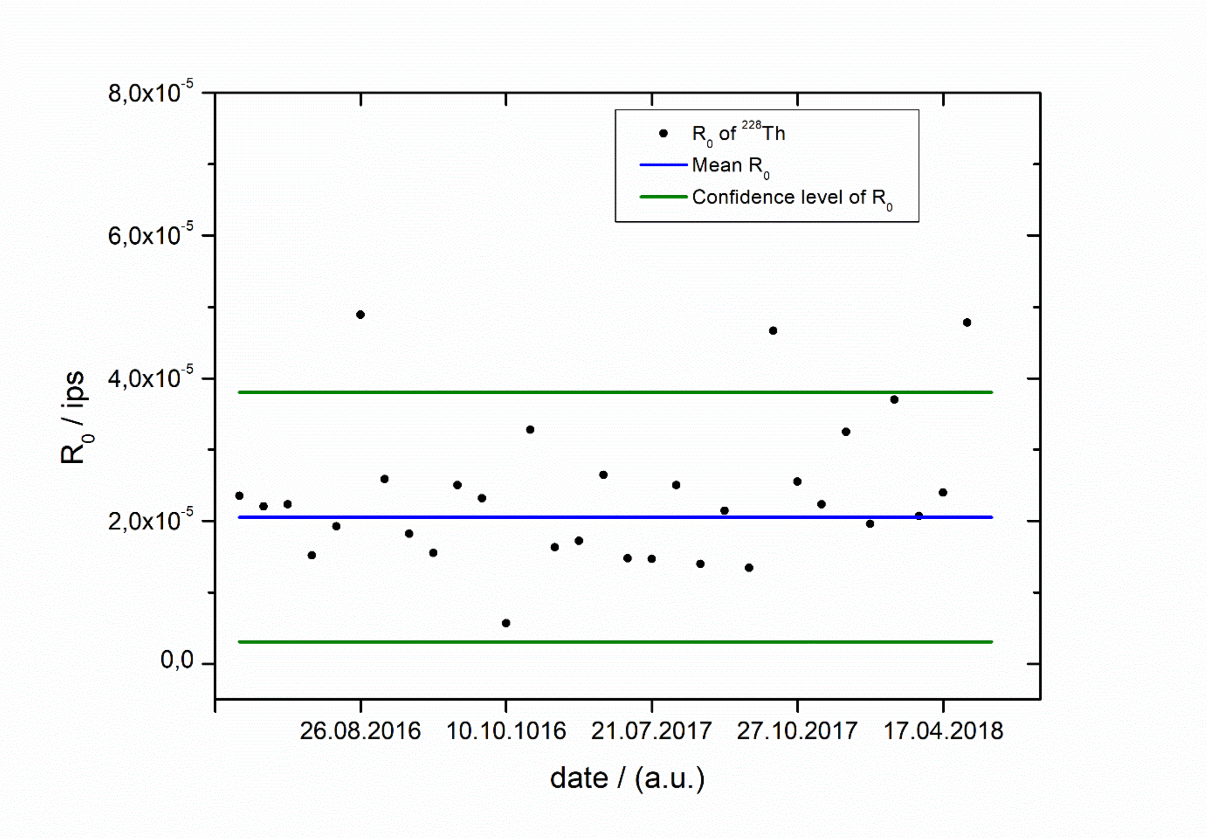

Figure 3.3: Observation of the background counting rate (R_0) of the energy range of ^{228}Th in α-chamber No. 8. Confidence level of 95%.

This kind of increased background rates could be caused by a contamination of the α-chamber due to radionuclides on the inner wall of the chamber. These residues of the former measurements are known as recoil nuclei [3]. During an α-decay process, the remaining core leaves the steel chip, which was used as supplement, and remains on the inner wall of the chamber. There it stays and the further α-decay could be detected during the background observation. By measuring high active samples, the recoil nuclei become more recognizable in the following background spectrum. Figure 3.4 shows the background counting rates for the energy range of ^{228}Th in chamber No 2.

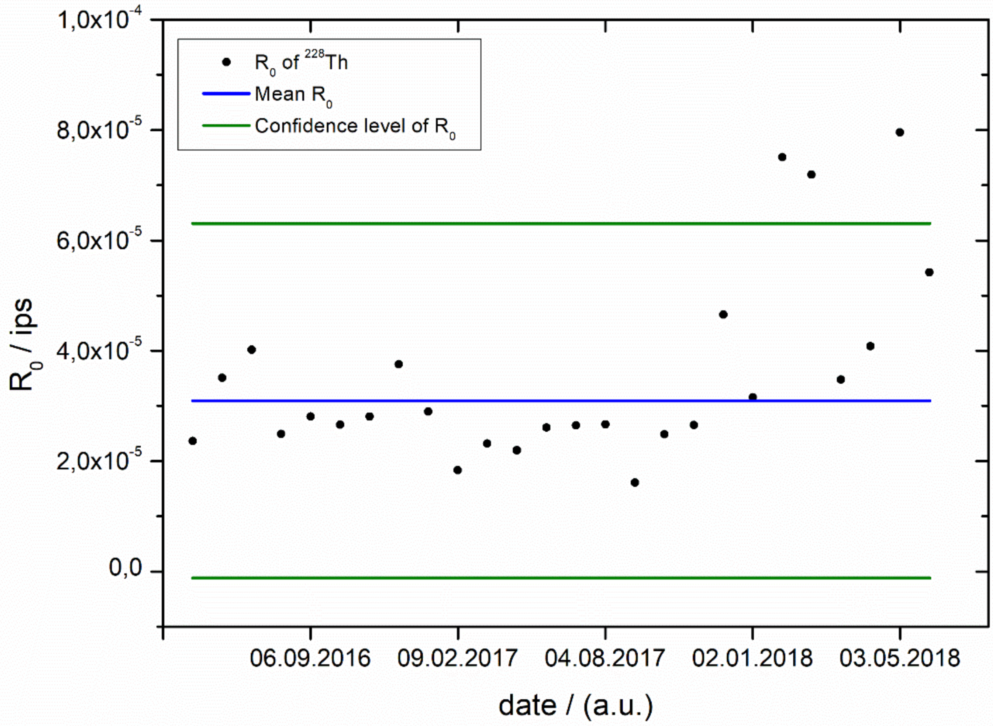

Figure 3.4: Observation of the background counting rate (R_0) of the energy range of ^{228}Th in α-chamber No.2. Confidence level of 95%.

The counting rates increased at the end of the year 2017 and stayed at increased levels since then. Reason for that was the use of a different thorium tracer for yield determination. Before 2018 we used the tracer ^{229}Th, which did not show increased background counting rates. Since the end of 2017 the tracer ^{227}Th was used. The decay products of ^{227}Th emitted recoil nuclei, which emitted α-particles within an energy range [3] which was partly used for evaluation of ^{228}Th. Thus, the background increased. However, in these cases some time was waited until the recoil nuclei decayed and the following measurement could be proceeded without interferences.

Energy calibration

In advance of each measurement, an energy calibration had to be performed. This was achieved by measuring a supplement with three electrodeposited radionuclides, which decay with known α-particle energies. Three peaks were formed during the calibration measurement and the calibration was done by assigning the channels of the peak maxima to the respective known energy values. Equation 15 gives the linear relation of energy (E) and channels (C). E_0 is the y-intercept and β is the slope of the linear calibration curve.

$$E = E_0 + \beta \cdot C \tag{15}$$

The used radionuclides for the energy calibration were ^{239}Pu, ^{241}Am and ^{244}Cm with the energy values 5.157 MeV, 5.486 MeV and 5.805 MeV, respectively [4]. The mean of the curve parameters of all energy calibrations done during the last three years is shown in Table 3.6.

Table 3.6: Overview over the energy calibrations done in the last three years. The values E_0, β, the relative standard deviation (RSD) of E_0 and β of all four chambers are shown.

Chamber No.	**E_0 / MeV**	**RSD of E_0**	**β / (MeV / Channel)**	**RSD of β**	**Number of calibrations**
2	2.86	0.8%	0.0046	0.8%	58
6	2.98	0.7%	0.0048	1.1%	46
7	2.95	1.4%	0.0048	1.4%	39
8	3.47	0.5%	0.0055	0.8%	33

There was no significant shift concerning the channel-energy response of the certain detector chambers. The relative standard deviation was under 1.4% in all cases. Thus, a reliable measurement set-up for α-counting was ensured and all peaks of the measured spectra could be identified unambiguously in the evaluations.

ICP-MS

The parts of the ICP-MS, which were located in the interface region showed deterioration due to the high temperatures in this region during operation. It was necessary to monitor the performance per working day to ensure reliable working conditions. This was done on the basis of a certified solution provided by PerkinElmer, namely SmartTune solution. This solution contained 10 ppb of the elements Ba, Be, Ce, Co, In, Pb, Mg, Rh and U. This solution was analyzed using a prefabricated routine. If the outcome complied defined values, the performance test was successful. The defined values, the analyzed elements and the reason for monitoring are shown in Table 3.7.

Table 3.7: Thresholds for the daily performance check values

Measured mass / amu	Element	Value	Performance criteria
23.985	Mg	> 100,000	Sufficient counts for elements of all mass ranges
114.904	In	> 400,000	
238.05	U	> 300,000	
68.9525/137.905	(Ba^{++}/ Ba)	< 3%	Prevention of double positive charged ion generation
155.9/139.905	(CeO/Ce)	< 3%	Prevention of oxide generation
220	-	< 30	Check for detector functionality

In case of a failure of the daily performance test, a trouble shooting procedure needed to be done. Several instrument parameters, such as argon flows, calibration of the ion optic, mass calibration, detector voltage and detector calibrations were optimized using certified solutions until the daily performance test was passed. All ICP-MS measurements in this thesis were conducted after a passed test to guarantee the reliability of the data.

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4. Results and discussion

4.1 Age determination of young ivory to continue the calibration curves for the radionuclides ^{14}C, ^{90}Sr and $^{228}Th/^{232}Th$

This chapter was published in Forensic Science International. Additional unpublished data were added, which were produced after publication. The unpublished data were produced by analyzing ivory to complete the calibration curves presented in this chapter. The results deriving from these data were made from ivory samples labeled with No. 13-20 in the experimental part. The layout specifications of the journal were changed for uniformity reasons.

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Abstract

The age determination of elephant ivory provides necessary and crucial information for all criminal prosecution authorities enforcing the Convention on International Trade in Endangered Species of Wild Fauna and Flora. The knowledge of the age of ivory allows to distinguish between pre-convention, hence legal material and ivory deriving from recent, illegal poaching incidents. The commonly applied method to determine the age of ivory is radiocarbon dating in the form of bomb pulse dating, which however will fade out soon. This work provides an enhancement of the radiocarbon dating method by supplementary determination of the isotope profile of ^{90}Sr and the two thorium isotopes ^{228}Th and ^{232}Th. This combined analysis allows for a precise and unambiguous age determination of ivory. We provided calibration curves for all involved radionuclides by analyzing ivory samples with known age and investigated a new method for the extraction of strontium from ivory.

4.1.1 Introduction

The number of wild elephants is decreasing rapidly in recent times. In 2016, only roughly more than 350,000 specimens of the African elephant were left in eighteen African countries [1]. The current rate of decrease is eight percent, accounting for roughly 28,000 elephants per year [1]. This is due to the fact that elephants are poached for their tusks, which consist of ivory. The so-called “white gold” appears on international markets in raw as well as processed form. The elephant poaching industry is fueled by high prices and a large profit to be gained. The Convention on International Trade in Endangered Species of Wild Fauna and Flora (CITES), which lists all protected animals and plants, aims to ensure that international trade in specimens of wild animals and plants does not threaten their survival. Hence, it regulates and controls the international trade on animal products, including elephant ivory. The Convention entered into force in the year 1975 and currently has 183 parties, which shows a wide-spread international acceptance. According to CITES Resolution Conference 13.6 [2], the date from which the protection of the Convention applies to a specimen is the date when the species was first included in one of the Convention’s appendices. While the Asian elephant (*Elephas maximus*) was listed for the first time on 1 July 1975, the African elephant (*Loxodonta Africana*) followed on 26 February 1976. Accordingly, the international trade of elephant ivory younger than these dates is prohibited, but certain exceptions are defined in the Convention as well. However, since 1990 no fresh raw ivory could have entered international markets legally. To enforce the Convention’s regulations, an accurate determination of the age of elephant ivory provides necessary and crucial information for criminal prosecution authorities of all countries which signed the Convention.

The commonly used method for age determination is radiocarbon dating, which was investigated from 1950 to 2010 by Hua et al [3, 4]. They created calibration curves for the age dependence of the ^{14}C content in organic matter. The curves showed that unambiguous age determination by solely applying radiocarbon dating is insufficient, since it can generate ambiguous findings. Moreover, the bomb pulse curve will fade out soon. To overcome this drawback, we developed a combined analysis of ^{14}C [5, 6], ^{90}Sr [5, 7] and $^{228}Th/^{232}Th$ [8, 9] for an unambiguous and precise age determination of ivory tissue. The advantage of the combined analysis was the huge amount of additional information gained yet having a low consumption of ivory tissue. The procedure was optimized for a time-saving and cost-efficient analysis of radionuclides by separation and subsequent detection with low-level radioactivity measurements.

Although the analysis time for ivory tusks could be reduced by the combined method, further investigations in this direction were needed. Hence, we used the crown ether resin SrSpec™ for the analysis of ^{90}Sr. Since their first investigation in the year 1967 [10], crown ethers were used for selective separation of metal ions. In the case of SrSpec™ some limitations in functionality and selectivity due to high amounts of calcium in ivory samples had to be overcome. In combination with the pre-separation of calcium with 1-pentanol, it was possible to develop a new much less time-consuming but powerful method for the separation of strontium from all other disturbing radionuclides.

Besides the new analytical procedure, we created calibration curves for all evaluated radionuclides by analyzing ivory samples of known age. It was possible to expand the calibration curves from earlier studies [11] until the year 2018 by analyzing ivory with an age of 20 years or less. These calibration curves allowed for the clear age determination of unknown ivory tissue. The new developed method is already well-established in the private and jurisdictional sector and we provide our calibration curves on www.ivoryID.org. In this work, we present the updated calibration curves, the new extraction technique for ^{90}Sr and finally the procedure of our ivory dating by means of an applied example.

4.1.2 Experimental

The method used for the ^{14}C and ^{228}Th/^{232}Th determination was developed by our group and is already described in the literature [5, 8]. The aspects of the recently developed method for the strontium analysis are further described in this chapter. In the first step, five grams of raw ivory sample were crushed and incinerated at 650°C in a muffle furnace. To remove all remaining organic compounds, the ivory ash was dissolved in concentrated nitric acid and evaporated to dryness [5]. In a second step, the removal of alkali metals via oxalate precipitation was done [12, 13]. For this purpose, the ivory ash was dissolved in 3 M nitric acid and 70 mg of strontium nitrate were added as tracer. After filtration of the insoluble components, five grams of oxalic acid dihydrate were added to the solution and the pH value was adjusted to a value of 5 - 6 with ammonia solution. After a centrifugation step, the oxalate precipitate was dissolved under heat at 100°C with 20 mL of 6 M nitric acid. In the third step, the high amount of calcium was removed from the sample with 1-pentanol [14, 15]. Two distillations were performed to achieve the separation of strontium and calcium. After cooling the solution to ambient temperature, 40 mL of 1-pentanol were added and the distillation was started. The strontium precipitate was removed after each distillation step from the 1-pentanol solution, which was saturated with calcium. In the fourth step, the complete separation of strontium from all other disturbing nuclides was performed with the resin SrSpec™. Therefore, a glass column (inner diameter: 10 mm) was filled with three grams of SrSpec™ resin [10, 16, 17, 18]. The column was conditioned with 2 free column volumes (fcv) 6 M nitric acid, 2 fcv 0.1 mM nitric acid and 2 fcv 6 M nitric acid. The sample uptake was done with 5 fcv 7 M nitric acid. The column was washed with 5 fcv 6 M nitric acid, 1 fcv 1 M nitric acid and 1 fcv 0.1 M nitric acid. The strontium elution was done with 0.1 mM nitric acid. A low-level β-counter was used for the radiochemical measurements of ^{90}Sr. The total amount of calcium in the ivory sample was determined photometrically by a calcium cell test and a photometer.

The chemicals we used to perform the ^{90}Sr analysis were nitric acid (Fisher Scientific International Inc., Schwerte, Germany), strontium nitrate (Fluka Inc., Buchs, Switzerland), oxalic acid dihydrate (Merck KGaA, Darmstadt, Germany), concentrated ammonia solution (Merck KGaA, Darmstadt, Germany), 1-pentanol (Merck KGaA, Darmstadt, Germany) and SrSpec™ resin (50-100 µm, Triskem International, Bruz, France). The p.a. grade chemicals were used without further treatment. We used a furnace model Thermicon T (Heraeus Holding GmbH, Hanau, Germany) for the incineration of the ivory samples. A low-level β-counter Berthold LB 770-2 (Berthold Technologies, Bad Wildbad, Germany) was used for the measurements. A calcium cell test 100858 (Merck KGaA, Darmstadt, Germany) and a photometer Spectroquant Nova 60 (Merck KGaA, Darmstadt, Germany) were used for the calcium determination. The ivory samples analyzed within this study are described in Table 4.1.

Table 4.1: The data of the ivory samples used in this study. The date of sample drawing, the analyzed mass of raw ivory and the source of supply are shown.

Code	**No.**	**Sample drawing**	**Analyzed mass of raw ivory / g**	**Source of supply**
195	1	20.05.2010	12.4	Zoological garden Wuppertal
202	2	01.07.2010	10.6	Zoological garden Wuppertal
196	3	19.07.2011	7.7	Zoological garden Wuppertal
193	4	01.07.2012	11.6	Zoological garden Basel
194	5	15.10.2012	13.0	Zoological garden Wuppertal
197	6	23.01.2013	10.3	Zoological garden Wuppertal
198	7	25.01.2013	9.7	Zoological garden Wuppertal
199	8	10.04.2014	10.1	Zoological garden Wuppertal
200	9	01.07.2014	9.4	Zoological garden Wuppertal
201	10	01.07.2015	10.7	Zoological garden Wuppertal
207	11	09.01.2016	13.5	Zoological garden Wuppertal
206	12	03.02.2016	10.6	Zoological garden Wuppertal
260*	13	08.01.2005	11.3	Zoological garden Basel
262*	14	11.08.2012	12.4	Zoological garden Basel
263*	15	14.02.2013	10.8	Zoological garden Basel
266*	16	18.02.2016	11.0	Zoological garden Basel
268*	17	20.04.2017	10.2	Zoological garden Basel
269*	18	03.01.2018	10.8	Zoological garden Basel
270*	19	09.11.1998	9.8	Zoological garden Basel
271*	20	14.08.2003	13.8	Zoological garden Basel

*unpublished

4.1.3 Result and discussion

The calibration curves in this chapter were generated by using the analytical methods described in the experimental part. In this work, the data gap for the analyzed radionuclides for death time later than 2000 was filled. The calibration curve of ^{14}C is shown in Figure 4.1. Reference data from the literature (B) and data from former studies from our group (blue) were added for comparison. The calibration curve from Hua and Barbetti [3, 4], which ends before 2000, was completed during this work with ivory samples newer than 2000 (green - A). The ^{14}C content was calculated as percent modern carbon, which is an internationally acknowledged and time-independent value [19] representing the specific activity of ^{14}C. After the atomic bomb tests, which took place after the year 1952, the pMC value in ivory increased due to neutrons released by the explosions [20] and reached a maximum in 1965. An unambiguous age determination only relying on ^{14}C determination is not possible, since there are always two possible time frames with equal plausibility for one pMC value. Moreover, the pMC value will decrease in the future to a value of around 100, such as it was before the bomb tests. Therefore, a distinction between ivory older than 1952 and fresh ivory will not be possible anymore. Hence, the analysis of additional radionuclides as described in the following part, is necessary.

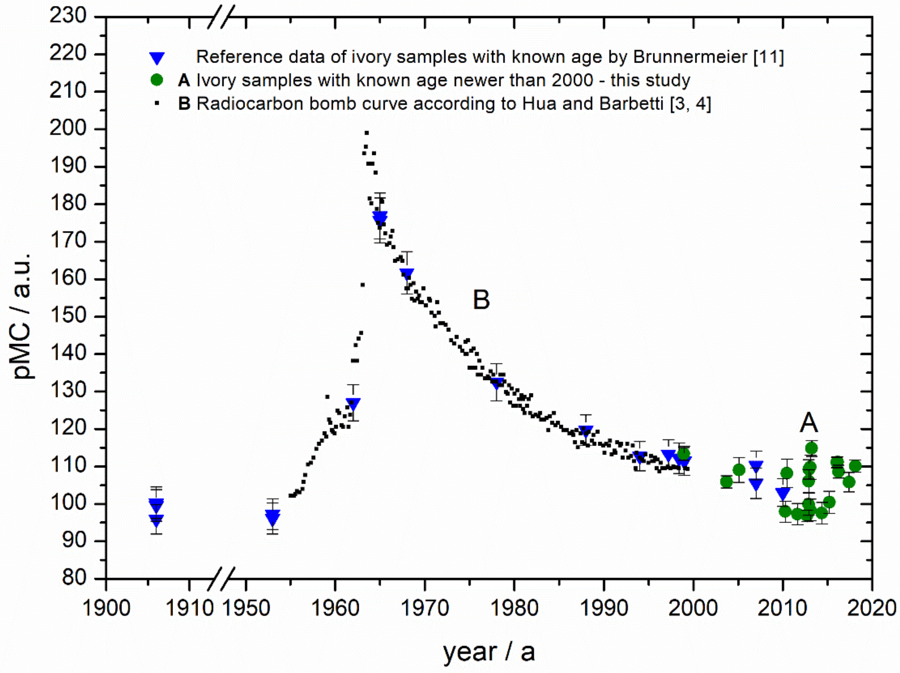

Figure 4.1: Calibration curve of the time dependency of the ^{14}C content in ivory. pMC values of independently dated ivory (green – A and blue [11]) are shown. Literature data were added for comparison (black - B) [3, 4].

A subsequent determination of ^{90}Sr was done to narrow the correct time frame. ^{90}Sr is an artificial isotope, which was formed during the atomic bomb tests in the sixties [21]. Figure 4.2 shows the ^{90}Sr content in human bone (D) [22] and the ^{90}Sr content of analyzed ivory in this (C) and former studies [23]. The content of ^{90}Sr in human bones and ivory is influenced by the atomic bomb explosions in a similar way, since a maximum can be found in 1965 in both curves. The fact that the ^{14}C curve in Figure 4.1 exhibits a maximum at the same position shows that the content of ^{14}C and ^{90}Sr was affected in a similar way by the explosions. However, the ^{90}Sr content in ivory could be used for the purpose of age determination. Ivory with a ^{90}Sr activity significantly higher than our limit of detection (0.003 Bq / g Ca) was extracted from elephants that died after 1952, because they had to be still alive at this date to incorporate the artificial ^{90}Sr. Considering the error bars for ^{90}Sr in ivory newer than 1965, two data clusters can be observed, which are indicated by two different calibration curves. There is a data cluster with higher ^{90}Sr activities (dotted curve) and one with lower ^{90}Sr activities (dashed curved). This fact could be caused by the different natural habitats of the elephants and thus different incorporation of ^{90}Sr. The atomic bomb tests mostly took place in the northern hemisphere, where the ^{90}Sr activity is expected to be higher compared to the southern hemisphere. Hence, a possible explanation for the two data clusters could be the origin of the animals. To prove this assumption, more investigations must be done with independently dated ivory samples of known origin.

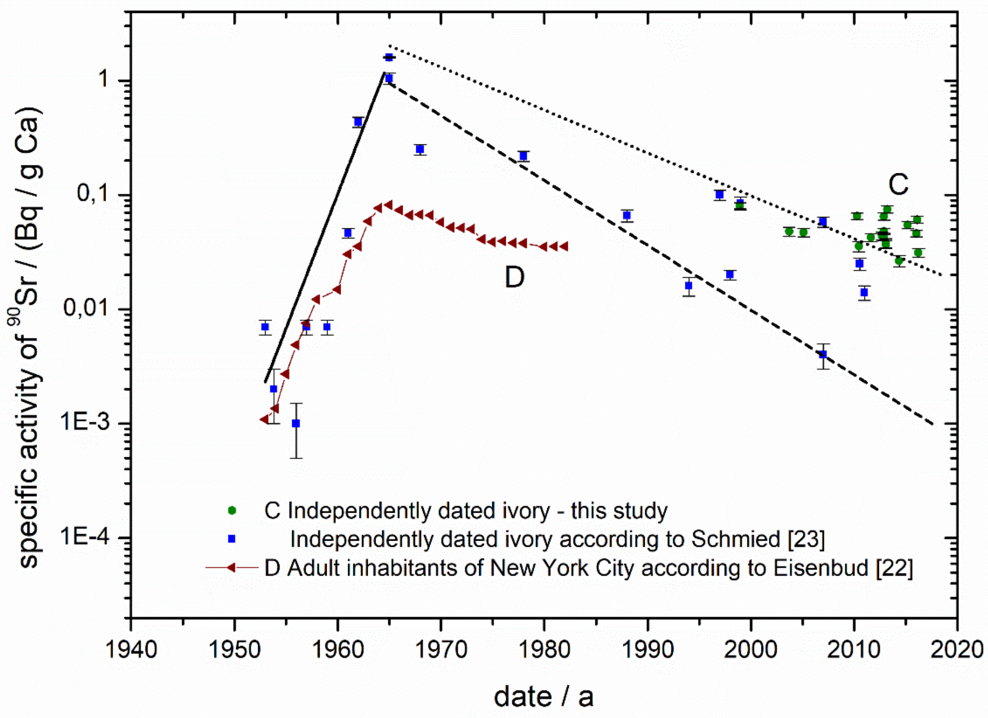

Figure 4.2: Calibration curve for the ^{90}Sr content in ivory samples. ^{90}Sr in independently dated ivory data from this work (green - C). Literature data from Eisenbud (red - D) were added for comparison [22].

The newly developed method for the extraction of ^{90}Sr from other nuclides based on the high selectivity of the crown ether 4',4"(5")-di-tert-butyldicyclohexano-18-crown-6 bound in an Amberchrom™ substrate [24]. This separation method facilitated a faster (working time about 5 h), safer and cheaper (20% savings) analysis of ^{90}Sr, compared to other methods in the literature [23, 25]. The procedure of the solid phase extraction is shown in the experimental part [18]. After loading the column with sample solution, it was possible to remove other falsifying nuclides (such as cesium, yttrium and calcium) using nitric acid with high concentration. Subsequently, strontium was eluted with 0.1 mM nitric acid. Extraction yields of 70 - 80% were obtained. The radiometric detection based on the radioactive equilibrium between strontium and yttrium (Figure 4.3). Therefore, the determination of the exact separation time of yttrium on the column was important. A further big advantage of this method was that the measurement of ^{90}Sr could be done with low-level β-counting as well as liquid scintillation counting.

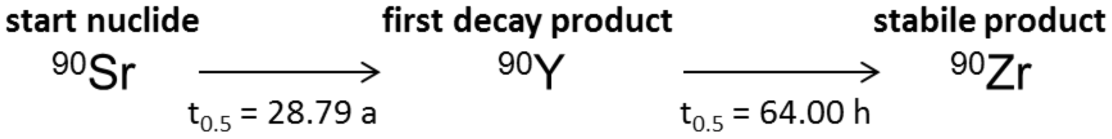

Figure 4.3: Radioactive equilibrium between ^{90}Sr and ^{90}Y, values for half-lives adapted from [26].

The ratio of the activity concentrations of ^{228}Th and ^{232}Th needed to be determined for further information about the sample, especially if there was still no clear age determination after ^{14}C and ^{90}Sr analysis. The calibration curve for the ratio ^{228}Th/^{232}Th in ivory, which was obtained in our work is shown in Figure 4.4. Since a time-dependent ratio was calculated, it was useful to introduce the post mortal interval value. This was the time difference between death of the elephant and the date of the analysis. The curve, which is depicted in Figure 4.4 is a calculated curve. ^{232}Th and ^{228}Th are part of the thorium decay series. ^{228}Th is formed from ^{232}Th over ^{228}Ra and ^{228}Ac as well as solely from ^{228}Ra, which is also a natural content in ivory. Assuming a ^{228}Ra content of 3.3 mBq per g ash weight, a well-fitting curve could be calculated. After the death of the elephant, the PMI value raises quickly due to the lower half time of ^{228}Th compared to ^{232}Th. After about 40 years, the radioactive equilibrium between the two isotopes is established and the value becomes one. Since the ratio changes quickly in the first years after death, the thorium analysis is useful for a very precise age determination of newer ivory in this time period. Moreover, since in the future the ^{90}Sr as well as the ^{14}C value will assimilate the values present before the bomb tests, the thorium analysis will become a crucial and indispensable technique for ivory dating, since it is not affected by the bomb tests. The uncertainties of the data points in Figure

4.4 seemed comparably high. This is due to the naturally low thorium concentration in ivory and thus a result of low yields.

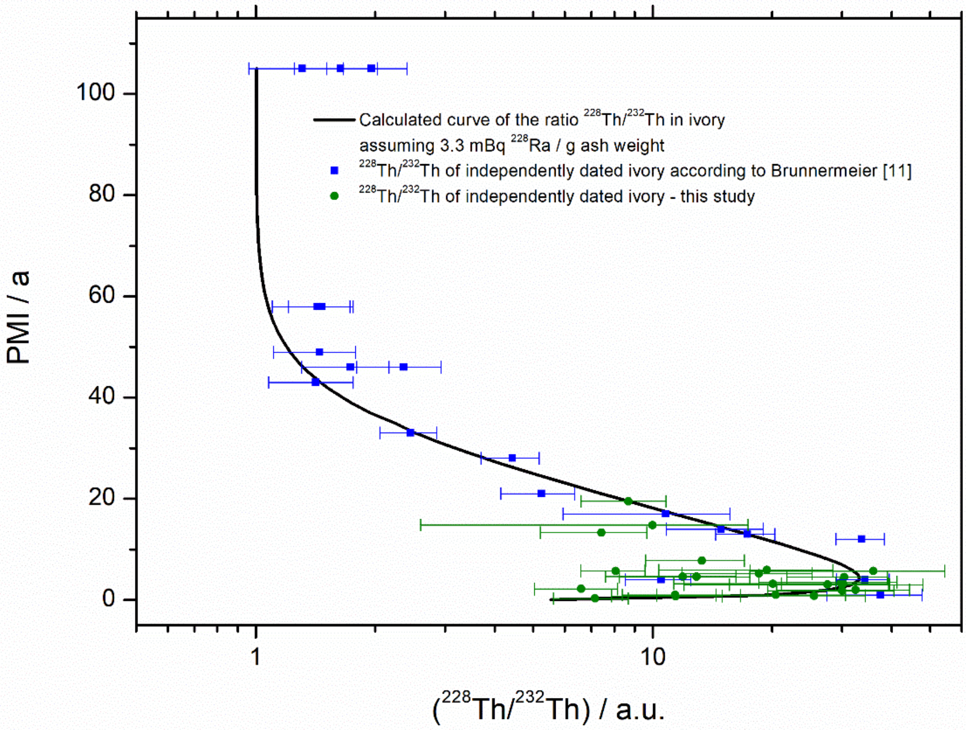

Figure 4.4: Calibration curve of the time dependence of the ratio ^{228}Th/^{232}Th in ivory. Data from former studies were added (blue) [11]. Fit curve was calculated by assuming 3.3 mBq ^{228}Ra / g ash weight.

An exemplary procedure for ivory dating of a real sample is shown in Table 4.2. In a first step, the ^{14}C determination was carried out. The shape of the ^{14}C calibration curve indicated two equally possible time frames. Hence, further analysis of ^{90}Sr and ^{228}Th/^{232}Th had to be done for a clear age determination. If there was a ^{90}Sr activity over the limit of detection, the elephant had to be still alive after 1956, because ^{90}Sr was only present in the environment after 1952 and hence could be incorporated by the animal via the food chain. The ivory had to be older than 1952 if no ^{90}Sr was detectable. Additionally, the thorium analysis was applied to identify the correct time frame. If the ratio of the activity concentrations of the thorium isotopes is significantly higher than one, the death of the elephant cannot be no longer ago than 40 years. Table 4.2 shows the results of the ivory dating as well as the made conclusions.

Table 4.2: Procedure of an exemplary ivory dating.

Radionuclide	Value	Unit	Conclusion / date		
^{14}C	126 ± 2	pMC	1962.4 ± 0.4	or	1982 ± 1
^{90}Sr	0.188 ± 0.005	Bq / g Ca	Not older than 1952		
^{228}Th/^{232}Th	6 ± 3	a.u.	Not 1962.4		

Only the ^{228}Th/^{232}Th determination allowed for an unambiguous age determination. In this example, the ^{14}C determination proposed two time frames, of which one indicated a legal ivory tusk (age 1962.4) and the other indicated a poached ivory tusk (age 1982). It is shown here that the combined analysis is indispensable for a clear age determination and a successful prosecution, if necessary.

4.1.4 Conclusion

We developed a reliable method for the unambiguous age determination of ivory by improving the common radiocarbon dating. The analysis of the isotopes ^{14}C, ^{90}Sr, ^{232}Th and ^{228}Th were used to overcome the drawback of a single ambitious radiocarbon analysis. Moreover, this method can also be applied in the future, whereas the solely ^{14}C bomb pulse dating will not be applicable anymore. We updated the calibration curves which enabled the precise dating of very recent ivory. With this dating method, we made a further step towards the preservation of one of the most iconic and threatened species worldwide by distinguishing between legal and illegal ivory.

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4.2 Long-term study on the change of the ratio ^{228}Th/^{232}Th in ivory over time

4.2.1 Introduction

The number of extinct species is growing every day. Various factors, such as climate change [1] and the demand for animal products [2], are a threat for the survival of many species. The elephant, which is probably the most iconic animal representing the African fauna, shows an exemplary decline of animal numbers all over the world [3]. The high prices and the large margins of profit for the valuable ivory tusks fuel the elephant poaching industry and the illegal ivory trafficking. The authorities of all countries are forced to act to ensure the survival of the elephants and various other animals. The Convention on International Trade in Endangered Species of Wild Fauna and Flora was signed by almost all countries in the world [4]. As consequence, a law was enforced in the year 1975 in Germany, which restricts the trade of ivory material. Whereas ivory older than 1976 may be traded legally, the trade of ivory, which was taken from an elephant after 1976 is declared as illegal. A technique is in demand to distinguish legal (older than 1976) and illegal (newer than 1976) ivory. Schupfner and co-workers [5] developed a method, based on the analysis of radionuclides, for the age determination of ivory material. A combined analysis strategy is used for a reliable and unambiguous ivory dating. The radioisotopes ^{14}C, ^{90}Sr and the ratio of the thorium isotopes ^{228}Th and ^{232}Th are determined, which enables the unambiguous age determination process. The activity profiles in the environment of the isotopes ^{14}C and ^{90}Sr, both affected by the atom bomb testing phases in the middle of the 20th century [6], are widely investigated and calibration curves were created for ^{14}C [5, 7] and ^{90}Sr [5, 8], respectively. The ratio of the activity concentrations of ^{228}Th and ^{232}Th in ivory can be used as indication tool for recently poached ivory. The activity of the long-lived ^{232}Th in ivory can be assumed as constant over the years due to the long half-life [9]. The ^{228}Th activity changes significantly in the first years after the death of the elephant [5]. The natural content of ^{228}Ra in ivory decays over ^{228}Ac to ^{228}Th, which results in a high value for the ratio ^{228}Th/^{232}Th after death of the elephant. A maximum is reached after roughly four years [5]. After 40 years, which represent roughly seven half-lives of ^{228}Ra, the ^{228}Ra is mostly decayed and the ^{228}Th activity is predominantly defined by ^{232}Th, which decays to ^{228}Th over ^{228}Ra and ^{228}Ac, respectively. Hence, the ratio of ivory older than 40 years becomes and remains one. Therefore, a ratio ^{228}Th/^{232}Th significantly higher than one indicates an ivory sample, which is not older than 40 years and thus illegal. Figure 4.5 shows the time dependent development of the ratio of the activity concentrations of the isotopes ^{228}Th and ^{232}Th.

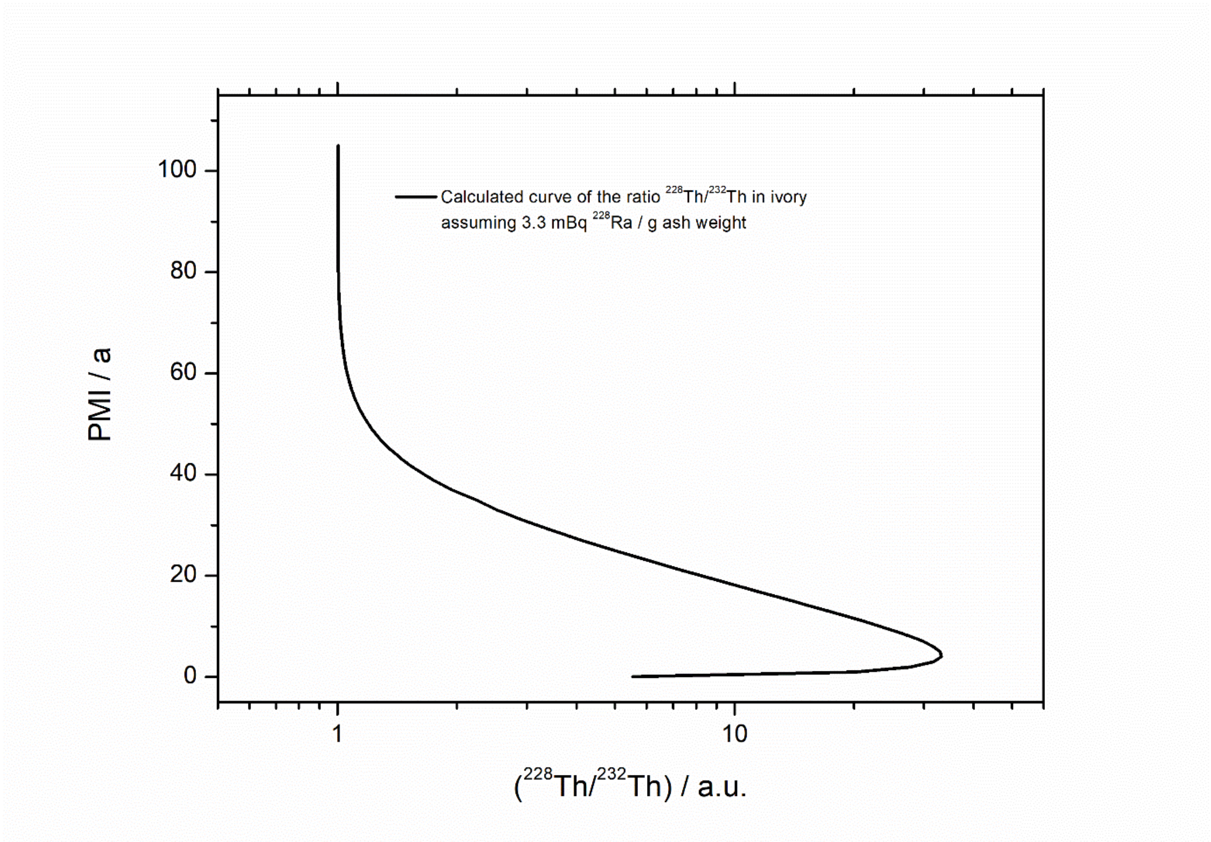

Figure 4.5: Calculated curve of the changing of the ratio ^{228}Th/^{232}Th in ivory. The post mortal interval (PMI) is the time difference between time of analysis and the time of death. Adapted from [5].

The technique of age determination via the ^{228}Th/^{232}Th ratio is based on theoretical calculations, which are verified by the creation of a calibration curve via the analysis of independently dated ivory in chapter 4.1 [5]. However, a further validation of the created calibration curve can be achieved by the repeated analysis of the same ivory material after a passed period of time. After half a year, the change of the thorium ratio should be significant. An increase of the ratio (ivory not older than four years) and a decrease of the ratio (age between four and 40 years) can be expected. This work provides a study about the ^{228}Th/^{232}Th ratio changing of ivory samples over a certain time period. Suitable ivory samples were collected from zoological institutions and the thorium ratio was determined. The analysis was repeated after roughly half a year. The trend of the ratio changing was evaluated. Additionally, an ivory sample was analyzed four times within a period of two years to evaluate the ratio changing. Positive findings can validate the correctness of the calibration curve which improves the reliability of the age determination of ivory in the first years after the death of the elephant.

4.2.2 Experimental

The purity of the used chemicals was p.a. grade and the substances were used without further purification. Concentrated sulfuric acid, concentrated hydrochloric acid and concentrated ammonia were purchased from VWR (Ismaning, Germany). Chromosorb® W-AW-DMCS was purchased from CS-Chromatographie Service GmbH (Langerwehe, Germany). TEVA® resin was purchased from Triskem International (Bruz, France). Concentrated nitric acid, aluminum nitrate nonahydrate and trioctylphosphine oxide were purchased from Merck (Darmstadt, Germany). The specifications of the ivory material and the conducted measurements are shown in Table 4.3 and Table 4.4.

Table 4.3: Specifications of the ivory samples, whose analysis were repeated after half a year. Samples were received from the zoological garden of Basel.

Measurement	**Measurement Date**	**Age at measurement date / a**	**Analyzed mass of ivory ash / g**	**Sample drawing (Code)**
1st run				
1.1	03.05.2018	7.8	6.33	29.07.2010 (261)
2.1	29.05.2018	4.6	5.73	10.10.2013 (265)
3.1	18.05.2018	2.2	5.86	18.02.2016 (266)
4.1	14.04.2018	1.0	5.43	20.04.2017 (268)
5.1	15.04.2018	0.25	5.85	03.01.2018 (269)
2nd run				
1.2	20.11.2018	8.3	5.89	
2.2	20.11.2018	5.1	5.05	
3.2	20.11.2018	2.8	7.11	
4.2	22.11.2018	1.6	6.85	
5.2	20.11.2018	0.85	5.22	

Table 4.4: Specifications of the ivory sample, which was analyzed four times within two years. The sample was taken from the elephant on the date 09.01.2016 (Code 207). The sample was received from the zoological garden of Wuppertal.

Measurement	Measurement Date	Age at measurement date / a	Analyzed mass of ivory ash / g
6.1	16.11.2016	0.85	7.19
6.2	21.07.2017	1.5	8.69
6.3	04.09.2017	2.7	8.96
6.4	21.11.2018	2.9	5.47

The procedure of the analysis including sample preparation and measurement is already described in the literature [5]. The procedure is shortly summarized in this chapter. The raw ivory was incinerated and treated with concentrated nitric acid and concentrated hydrochloric acid to remove all organic compounds. The remaining ivory ash was used for two consecutive solid phase extraction procedures. The first column material was trioctylphosphine oxide impregnated on Chromosorb®. The second column material was TEVA® resin. The resulting eluate was free of matrix and disturbing radionuclides, which would interfere in the α-measurement, were removed. The thorium was electrodeposited onto a steel chip and measured via an α-spectrometer. The parameters of all measurements are given in Table 4.5.

Table 4.5: Measurement parameters of the α-spectrometric measurements.

Measurement	Measurement time / s	Measurement	Measurement time / s
1.1	410,000	4.2	600,000
1.2	270,000	5.1	420,000
2.1	340,000	5.2	270,000
2.2	270,000	6.1	420,000
3.1	320,000	6.2	440,000
3.2	600,000	6.3	600,000
4.1	430,000	6.4	410,000

4.2.3 Result and discussion

The analyzed ivory samples were provided by the zoological gardens of Wuppertal and Basel. The date of the sample drawing from the elephant was well known and provided together with the sample itself. The knowledge about the age of the samples was crucial for this study, since the expected thorium ratio changing only significantly takes place within the first 30 years after ivory extraction from the elephant. After 30 years (Figure 4.5), the ratio still changes, but the changing is slow and would be only be recognizable after waiting several years between the analysis. Hence, it was crucial to obtain ivory samples with known age and an age of not older than 30 years. According to the calibration curve in Figure 4.5, a trend of the ratio changing could be predicted. A summary about the expected results is shown in Table 4.6. Each line represents the repeated measurements of one sample after a certain period.

Table 4.6: Expected results of the changing of the ratio ^{228}Th/^{232}Th for repeated analysis.

Sample	**Sample drawing**	**Period between analysis and sample drawing / a**	**Expected trend of ^{228}Th/^{232}Th changing**
1	29.07.2010	0.55	Decrease
2	10.10.2013	0.48	Decrease
3	18.02.2016	0.51	Increase
4	20.04.2017	0.61	Increase
5	12.01.2018	0.60	Increase
6	09.01.2016	0.7, 1.8 and 2.0	Increase*

* The sample was analyzed four times within two years. The expectation about the ratio changing is an increase for all cases, since the sample is not older than four years at the date of the last measurement.

The expectation concerning the ratio changing was based on the known age of the sample. Sample 1 and 2 were older than four years, hence the maximum of the ^{228}Th/^{232}Th ratio in Figure 4.5 should be already passed and the decrease to a value of one should already be ongoing. The samples 3 – 6 were not older than four years, which means that their ^{228}Th/^{232}Th ratio should increase. For analysis, the ivory was crushed and two (four in case of sample No. 6) aliquots were formed. One was analyzed and the second was stored with air exclusion in a dry and dark drawer. The outcome of the experiments with samples 1 - 5 is shown in Table 4.7. The values of the activity concentrations of ^{228}Th and ^{232}Th, the ratio of ^{228}Th/^{232}Th and the uncertainty of the ratio ^{228}Th/^{232}Th are shown.

Table 4.7: Overview over the results of the determination of the ratio ^{228}Th/^{232}Th. Activity concentrations are given in mBq per gram ivory ash.

	1st run			**2nd run**		
Sample	**a (^{228}Th)**	**a (^{232}Th)**	**^{228}Th/^{232}Th**	**a (^{228}Th)**	**a (^{232}Th)**	**^{228}Th/^{232}Th**
1	0.67	0.05	13.0 ± 4	0.39	0.04	10.0 ± 3
2	0.55	0.04	13.0 ± 5	0.17	0.05	3.0 ± 1
3	0.24	0.04	6.0 ± 2	0.69	0.05	13.0 ± 4
4	0.72	0.06	11.0 ± 3	1.00	0.07	14.0 ± 3
5	0.24	0.03	7.0 ± 2	0.73	0.05	14.0 ± 3

Table 4.7 enables the comparison of the values of the activity concentrations of ^{232}Th for both runs. Since ^{232}Th has a very long half-life [9], the activity concentration of the first and the second run should not be differing. The relative uncertainties of the activity concentration values of ^{232}Th were at least 19%. Considering this uncertainty, the values of the activity concentration of ^{232}Th did not differ for independent analysis of the same sample with a waiting time of around half a year in between. The values of the activity concentration of ^{228}Th differed strongly in all cases, but that was expected due to the rather short half-life of ^{228}Th. The behavior of the ^{228}Th could be divided in two groups. The first two samples showed a decrease of the ^{228}Th activity concentration and the ^{228}Th/^{232}Th ratio, respectively. The ages of these samples at the first measurement date were 7.8 and 4.6 years, respectively. Hence, the expectation about the ^{228}Th/^{232}Th ratio changing in Table 4.6 was fulfilled. Both ratios decreased after a waiting time of roughly half a year. That verifies the assumption that after four years, the ^{228}Th activity in ivory decreases. The ages of the samples 3, 4 and 5 were 2.2, 1.0 and 0.25, respectively. An increase of the ^{228}Th activity was expected and the measurements could validate this assumption. In all three cases, an increase of the ^{228}Th activity and the ^{228}Th/^{232}Th ratio could be seen. Figure 4.6 shows the values of the measured ^{228}Th/^{232}Th ratios for the repeated analysis in the context of the calculated calibration curve in Figure 4.5. The calibration curve is given for comparison reason. Only the cutout for PMI values from 0 to 30 is shown. It can be seen that the trend predicted by the calibration curve was validated by the measurements. However, the values for the ^{228}Th/^{232}Th ratios for sample 1 and 2 differed strongly from the calibration curve. In this region, the curve depends strongly on the initial ^{228}Ra content in the ivory. A lower intake of ^{228}Ra of the elephant during lifetime could cause the low ^{228}Th/^{232}Th ratios in these samples.

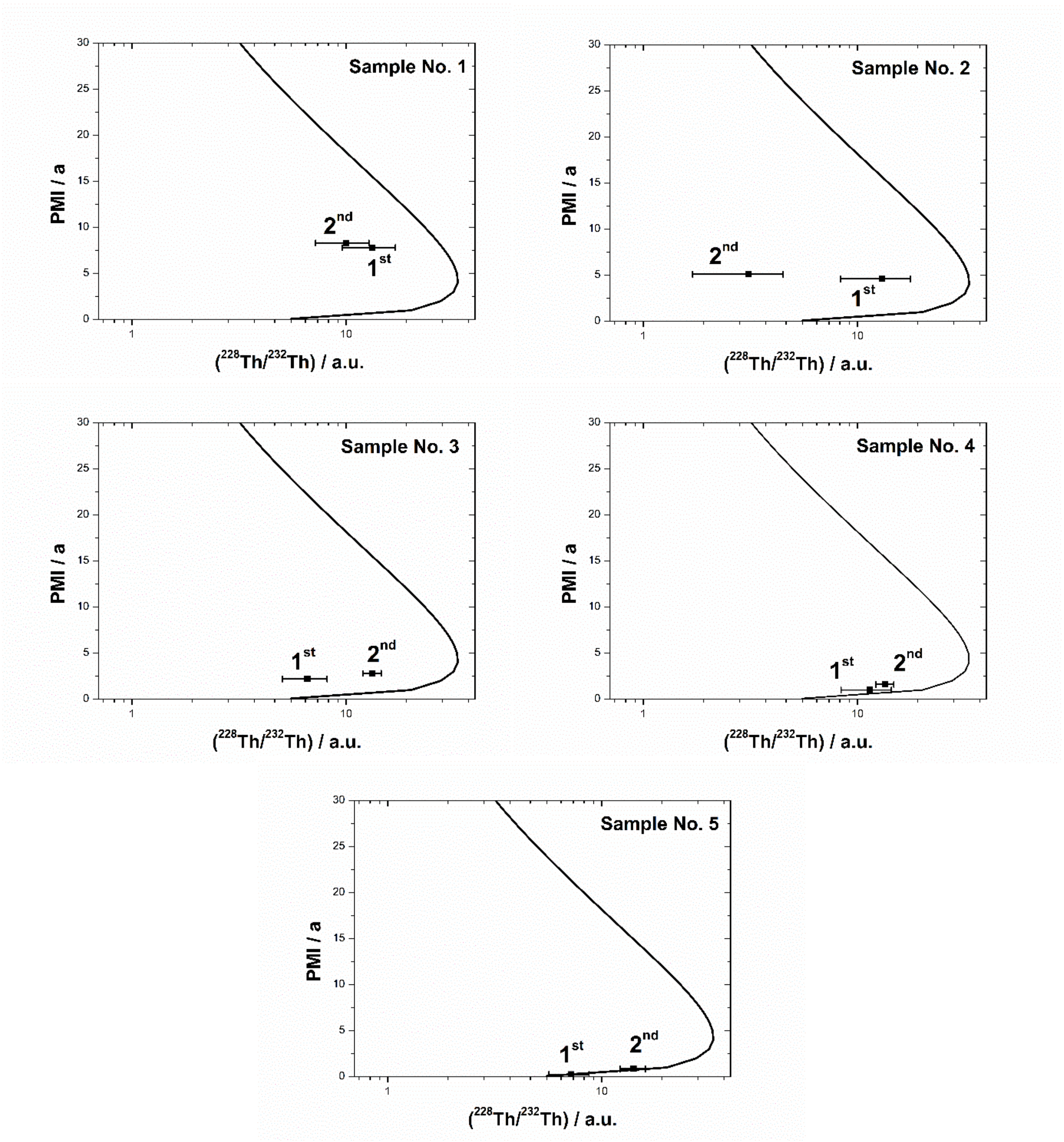

Figure 4.6: Depiction of the repeated analysis of the ratio ^{228}Th/^{232}Th of samples No. 1-5. Each graph represents the repeated analysis of one sample.

In addition to the five samples above, a series of experiments was done with the same ivory material (sample No. 6) over a period of two years. The thorium analysis was repeated several times and the resulting thorium ratios were compared. As described above, a steady increase for each further analysis was expected. The result for each measurement is shown in Table 4.8.

Table 4.8: Results of the long-time study over two years of repeated analysis of the same ivory material.

Measurement	$^{228}Th/^{232}Th$	Age at measurement date / a	Age difference vs previous measurement / a
1st	19 ± 5	0.8	-
2nd	20 ± 4	1.5	0.7
3rd	21 ± 3	2.7	1.2
4th	24 ± 7	2.9	0.2

The mean value of each further measurement increased as predicted. However, the uncertainties of each determination of the ratio $^{228}Th/^{232}Th$ overlapped with the mean values of other measurements. A trend for the ratio changing could be seen but the measurements showed uncertainties too high for the results to be unambiguous. Figure 4.7 shows the obtained results in comparison to the calibration curve in Figure 4.5. Except for the 3rd analysis, the mean values matched well with the calibration curve and gave an exemplary example for the $^{228}Th/^{232}Th$ changing within the first four years after death of the elephant.

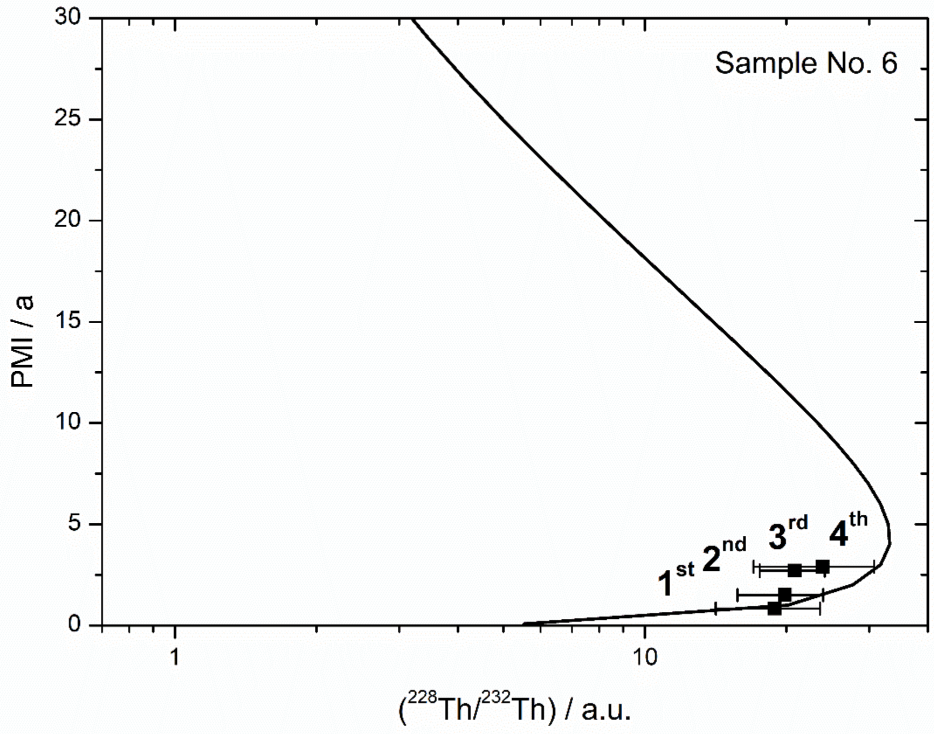

Figure 4.7: Results of the repeated $^{228}Th/^{232}Th$ analysis of the same ivory samples within two years.

The experiments showed that a repeated determination of the ^{228}Th/^{232}Th ratio provides further information on the age of the sample. Considering the curve in Figure 4.5, two possible PMI values for one ^{228}Th/^{232}Th ratio can be chosen. A value of 10 would indicate an age of about six months or an age of about 18 years. That is not relevant for the purpose of the age determination, since both ages would expose an illegal sample. However, the closer age of the sample would provide the law prosecution system with important information about the ivory trafficking and poaching incident. The repeated analysis would show which of the two possible ages is correct. An increase in the ^{228}Th/^{232}Th ratio would show that the younger age is correct and that the death of the elephant was recent. The part of the curve for low PMI values should be considered here. A decrease of the ratio would indicate that the older age is correct.

4.2.4 Conclusion

This study validates the predicted and calculated change of the calibration curve for the ratio of the activity concentrations of ^{228}Th and ^{232}Th. Six ivory samples were analyzed two or more times within half a year and two years, respectively. The mean values of the obtained ^{228}Th/^{232}Th ratio showed the changes which were predicted. Samples with an age lower than four years showed an increased ratio and samples with ages older than four showed a decreased ratio. The values did not always match the calculated curve perfectly, since the ^{228}Ra content differs for each elephant, but the trend of the change remained as predicted. This validity of the change enables the possibility to specify the age of the samples, since a single analysis always showed two possible ages for ivory not older than 40 years. That is of relevance for the criminal prosecution of the trafficking or the poaching incident. An issue was the rather high uncertainties of the ^{232}Th determination and the ^{228}Th/^{232}Th determination, respectively. A decreased of the uncertainties might be achieved by a combined determination via α-spectrometry and inductively coupled plasma mass spectrometry. That would enhance the age classification. This approached is discussed in the next chapter.

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4.3 Development of an analytical strategy for the determination of ^{228}Th and ^{232}Th in ivory based on the combined use of ICP-MS and α-spectrometry

This chapter was published in the Journal of Radioanalytical and Nuclear Chemistry. Table 4.15 was not published but added to demonstrate the improvement of the dating process for the samples 3-8. The layout specifications of the journal were changed for uniformity.

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Journal of Radioanalytical and Nuclear Chemistry (2018) 318: 2007-2011.

Abstract

Elephants are endangered due to the value of their ivory tusks. Therefore, a reliable method for age determination of ivory is of interest for the law enforcement against elephant poachers. The ratio of the activity concentrations of ^{228}Th and ^{232}Th can be used for the age assessment of ivory. In this report, the combination of two complementary detection techniques, namely inductively coupled plasma-mass spectrometry (ICP-MS) and α-spectrometry, for the determination of ^{228}Th and ^{232}Th in ivory is presented. Using ICP-MS in addition to α-spectrometry, the uncertainty of the ^{232}Th determination could be reduced significantly, which enabled a more accurate and effective ivory dating.

4.3.1 Introduction

The rapid decrease of the total number of elephants worldwide is a serious threat for their survival. The current rate of the annual decline is eight percent [1], accounting for roughly 28,000 elephants. This decrease is caused by poaching incidents, due to the huge profit for raw and processed ivory. The Convention on International Trade in Endangered Species of Wild Fauna and Flora (CITES) [2] aims for the protection of various animals from extinction by prohibiting the trade of animal products, which were poached after the date of the registration of the corresponding animal in the appendices of CITES. In the case of the African Elephant, it is the year 1976 [2]. Hence, a reliable and accurate method for ivory dating is in demand to distinguish between illegal and legal ivory. Schupfner and co-workers [3, 4] developed a method for ivory dating based on the radiochemical analysis of ^{14}C, ^{90}Sr and the ratio of the activity concentrations of ^{228}Th and ^{232}Th. The determination of the ratio ^{228}Th/^{232}Th is particularly attractive for the age assessment within the first 40 years after the death of the elephant, since the ratio ^{228}Th/^{232}Th changes significantly in this period [3, 5]. The ^{228}Th/^{232}Th ratio shows a maximum about four years after death of the elephant but decreases with time and approaches to one after 40 years [3]. This disequilibrium of ^{232}Th and ^{228}Th in ivory shortly after death of the elephant can be explained by the thorium radioactive series. ^{228}Th is formed from ^{232}Th over ^{228}Ra and ^{228}Ac. After death, ^{228}Th is predominantly formed by the decay of ^{228}Ra, which was incorporated by the elephant via food and water [3, 5]. After the death of the animal, the incorporation of ^{228}Ra stops and ^{228}Ra only decays to ^{228}Th over ^{228}Ac. Hence, the activity of ^{228}Th rises in the first years after death of the elephant [3]. After 40 years, which represents roughly seven half-lives of ^{228}Ra [5], the ^{228}Ra is mostly decayed and from there on ^{228}Th is mainly formed from ^{232}Th so that the value of the ratio ^{228}Th/^{232}Th becomes one. This applies for thorium, which is located at the pulpa [5], which is the part of the ivory tusk that is connected to the skull of the elephant and is supplied with thorium until the death of the elephant. However, the change of the ratio ^{228}Th/^{232}Th in the first 40 years after death of the animals can be used for age determination of the ivory. Since the signing of the agreement of CITES was roughly 40 years ago, this thorium analysis can serve to identify illegal ivory and is worth to be further investigated. The previously reported method by Schupfner and co-workers [3] is based on the α-decay of ^{228}Th and ^{232}Th and shows different uncertainties for the determination of both isotopes due to their different activities. Table 4.9 shows the typical situation of ^{232}Th and ^{228}Th in ivory concerning content and activity for three age ranges [3], as well as the corresponding concentrations after sample preparation.

Table 4.9: Overview over the contents, activities and the concentrations after sample preparation for the radionuclides ^{228}Th and ^{232}Th in ivory [3].

Radionuclide	**^{232}Th**			**^{228}Th**		
Age of ivory / a	**10**	**30**	**60**	**10**	**30**	**60**
µg Th / kg raw ivory	7.1	7.1	7.1	$2.2 \cdot 10^{-8}$	$3.1 \cdot 10^{-9}$	$1.0 \cdot 10^{-9}$
Concentration* / ppb	8.3	8.3	8.3	$2.6 \cdot 10^{-8}$	$3.6 \cdot 10^{-9}$	$1.1 \cdot 10^{-9}$
Activity* / mBq	0.3	0.3	0.3	7.9	1.1	0.3

*Corresponding to a typical mass of 12 g raw ivory used for the analytical determination. Concentration relates to a volume of 10 mL for the ICP-MS measurement.

^{228}Th shows a high activity for determinations by α-spectrometry, whereas ^{232}Th exhibits very low activities in ivory. This results in low counting rates for ^{232}Th and is associated with a high uncertainty for the determination of the ratio ^{228}Th/^{232}Th [5]. Hence, a complementary technique for a more reliable determination of ^{232}Th, such as inductively coupled plasma coupled with optical emission spectrometry [6] or mass spectrometry (ICP-MS) [7] is needed. ICP-MS proved to be a powerful and versatile technique for trace metal analysis [8 - 10]. In contrast to α-spectrometry, ICP-MS allows for small sample consumption [11, 12] and high throughput measurements [13, 14]. In addition, the efforts for sample preparation are considerably reduced in case of ICP-MS compared to α-spectrometry [15]. Although the limit of detection of ICP-MS is typically in the ppt range [16], ICP-MS is less attractive for some isotopes, such as ^{228}Th in ivory, as there are just sub-ppt concentrations of ^{228}Th present in the measuring solutions after sample pretreatment (see Table 4.9) [17, 18]. Consequently, it would be more favorable to determine ^{228}Th by α-spectrometry. The combination of α-spectrometry and ICP-MS seems to be an attractive concept in situations as described above for the analysis of ^{228}Th/^{232}Th. Becker et al. [19] investigated these complementary techniques to analyze uranium and plutonium ratios in soil samples.

The scope of this study was to demonstrate that ICP-MS and α-spectrometry can act as complementary techniques for the determination of ^{228}Th/^{232}Th ratios in ivory samples. It is shown that this method combination yields lower uncertainties for the determination of ^{228}Th/^{232}Th and hence can be used for a more reliable age determination of ivory.

4.3.2 Experimental

The purity of chemicals used was p.a. grade and the substances were used without further purification. Concentrated sulfuric acid, concentrated hydrochloric acid and concentrated ammonia were purchased from VWR (Ismaning, Germany). Chromosorb® W-AW-DMCS was purchased from CS-Chromatographie Service GmbH (Langerwehe, Germany). TEVA® resin was purchased from Triskem International (Bruz, France). The thorium and bismuth standard solutions were purchased from Spetec (Erding, Germany). Ultrapure concentrated nitric acid, concentrated nitric acid, aluminum nitrate nonahydrate and trioctylphosphine oxide were purchased from Merck (Darmstadt, Germany). The specification of the ivory material used this study is shown in Table 4.10. The analyzed ivory samples were all taken from the pulpa [5].

Table 4.10: Specifications of the used ivory material. The source of supply, mass of analyzed raw ivory, mass of ivory ash and the actual age of the samples are shown.

Code	No.	Source of supply	Mass raw ivory / g	Mass ivory ash / g	Sample drawing
BfN7	1	German Federal Agency for Nature Conversation	7.62	4.00	2005*
	2		7.55	3.96	
260	3	Zoo Basel	11.26	6.27	08.01.2005
261	4		11.43	6.33	29.07.2010
262	5		12.36	7.13	11.08.2012
263	6		10.78	5.51	14.02.2013
264	7		13.20	5.97	03.10.2013
265	8		11.49	5.73	10.10.2013

* Only the year of death of the elephant was known.

The α-spectrometric measurements were carried out using ion implanted silicon semiconductor detectors in an Octête α-chamber model U-034-1200-AS from EG&G Ortec (Meerbusch, Germany), which was controlled by the software Gamma Vision 5.1. An ICP-MS model ELAN 9000 from PerkinElmer (Rodgau, Germany) was used during this study. Data acquisition and evaluation were done with the ELAN Software 3.0. The parameters of the ICP-MS measurements are shown in Table 4.11.

Table 4.11: Instrumental parameters of the ICP-MS.

Instrumental parameter	Parameter setting
Nebulizer Gas Flow	0.57 L/min
Lens Voltage	5 V
ICP RF Power	1100 W
Analog Stage Voltage	-2000 V
Pulse Stage Voltage	1000 V
Discriminator Threshold	30 mV
AC Rod Offset	-8

The instruments and methods for sample preparation of ivory were already described in the literature [20, 21]. The procedure is shortly summarized in this paragraph. The raw ivory was crushed and incinerated at 650°C in an oxygen stream. The inorganic remains were used in two solid phase extraction procedures. The column materials were trioctylphosphine oxide impregnated on Chromosorb® and TEVA® resin, respectively. The eluate of the TEVA® column was free of matrix and disturbing radionuclides. This purified solution was used for the ICP-MS measurement. The liquid phase was first removed by evaporation, and the residue was dissolved in 1% nitric acid. The internal standard bismuth was added (15 ppb) and the solution was filled up to 10 mL with 1% nitric acid. The ICP-MS experiments were done with a ^{232}Th standard by measuring a volume of 10 mL with 15 ppb and 20 ppb of thorium after adding 15 ppb bismuth as an internal standard. The solutions were filtered using an 0.45 µm syringe filter prior to the measurements. Each measurement was repeated for three times. After the ICP-MS measurement, the remaining solution was used for electrodeposition to proceed with an α-spectrometric measurement. Measuring time for α-spectrometry was five days. The chemical yield was calculated via an added yield tracer ^{227}Th.

Since the reduction of the uncertainty concerning the ^{232}Th determination was crucial in this study, the used equations are described. The uncertainty (u_{Th232}) of the α-spectrometric measurement for ^{232}Th is defined according to Equation 16.

$$u_{Th232} = A_{Th232} \cdot \sqrt{\left(\frac{N0_{Th232}}{N_{Th232}}\right)^2 + \left(\frac{N0_{Th227}}{N_{Th227}}\right)^2 + (0.02)^2} \tag{16}$$

A_{Th232} is the obtained activity of ^{232}Th, N0 represents the background counts of the detector and N denotes the background corrected counts of the respective nuclides. The value 0.02 represents the uncertainty of the activity of the yield tracer ^{227}Th. The calculation of the uncertainty of ^{232}Th for the ICP-MS measurement was based on DIN 1319-3 [22]. The uncertainty was calculated as the root of the sum of the squared independent uncertainties. The independent variables were the signal of ^{232}Th, the signal of ^{209}Bi and the chemical yield.

4.3.3 Result and discussion

Analytical characterization of ICP-MS and α-spectrometry

The analysis time for one ICP-MS measurement including washing steps was as short as 1.7 minutes, which enabled the integration of ICP-MS measurements in the analytical procedure without significant loss of time. The ICP-MS determinations of ^{232}Th showed a good performance concerning linearity of the calibration curves ($R^2 = 0.998$) and the limit of detection (55 ppt). Moreover, it was found that for ^{232}Th determinations there were no isobaric or polyatomic interferences. Hence, reliable and precise measurements with relative uncertainties under 7% were possible. However, the used ICP-MS configuration was not sensitive enough for the ^{228}Th isotope, whose content is in a very low concentration range in ivory (Table 4.9). Although α-spectrometry was used for the measurement of both thorium nuclides, it showed much better performance for ^{228}Th since ^{228}Th had a significantly shorter half-life (^{228}Th: 1.9 a, ^{232}Th: $1.4 \cdot 10^{11}$ a [23]) and thus higher activity. The resulting relative uncertainties for the activity of ^{228}Th (< 14%) were smaller as for ^{232}Th (up to 67%). It seemed obvious to use both measuring techniques in a complementary way to reduce the uncertainties of ^{228}Th/^{232}Th determinations.

The compatibility of ICP-MS and α-spectrometry was tested using ^{232}Th standard solutions with 15 ppb and 20 ppb, respectively. The ICP-MS measurement was done first and the remaining solution was electrodeposited for the α-spectrometry. The results are shown in Table 4.12. The used equations for the uncertainties are described in the experimental section.

Table 4.12: Comparison of ICP-MS (n=3) and α-spectrometry using standard solutions with known concentration and activity.

ICP-MS			**α-spectrometry**		
Conc. / ppb	**Result / ppb**	**Relative Uncertainty**	**Activity / mBq**	**Result / mBq**	**Relative Uncertainty**
15	15.1	6%	0.61*	0.6	52%
20	21	7%	0.81*	0.8	13%

*Correspond to 15 ppb and 20 ppb, respectively. Calculated with 4.06×10^3 Bq / g ^{232}Th. Constants for calculation were adapted from [23].

The recoveries were 105% (ICP-MS) and 99% (α-spectrometry) for the 20 ppb standard solution and 101% (ICP-MS) and 98% (α-spectrometry) for the 15 ppb standard solution, respectively. Furthermore, the experiment showed that the relative uncertainties of the ICP-MS measurements of ^{232}Th were clearly lower than the relative uncertainties of the corresponding radiometric measurements. However, ^{228}Th had still to be determined via α-spectrometry, since the trace concentrations of ^{228}Th were below the limit of detection of the ICP-MS system.

Application of the newly developed method to ivory samples

Since the experiments with standard solutions proved the suitability of both techniques for the determination of ^{232}Th, the method was applied to ivory samples. The procedure of the sample preparation was applied as described in the experimental section. Eight ivory samples were analyzed and their ^{232}Th content was determined with ICP-MS and α-spectrometry. The results of the measurements are shown in Table 4.13. The results of the ICP-MS measurements were converted from concentration to activity to facilitate the comparison of the ICP-MS and α-spectrometry results.

Table 4.13: Results of the new measurement strategy applied to eight ivory samples. Activity concentrations (per gram ivory ash) refer to ^{232}Th.

No.	**ICP-MS** **a* / mBq**	**α-spectrometry** **a / mBq**
1	0.033 ± 0.002	0.03 ± 0.02
2	0.030 ± 0.002	0.04 ± 0.02
3	0.046 ± 0.004	0.05 ± 0.01
4	0.057 ± 0.005	0.05 ± 0.01
5	0.085 ± 0.005	0.08 ± 0.01
6	0.036 ± 0.002	0.04 ± 0.01
7	0.056 ± 0.005	0.05 ± 0.02
8	0.044 ± 0.004	0.04 ± 0.01

*Calculated with 4.06×10^3 Bq / g ^{232}Th. Constants for calculation were adapted from [23].

Within the limits of the uncertainties it was found that the results of both measuring techniques matched very well for all samples studied. Consequently, the ^{232}Th determination via α-spectrometry could be substituted by ICP-MS. Furthermore, the uncertainties of the determinations could be reduced significantly if ICP-MS was used in place of α-spectrometry.

Impact of the combined use of ICP-MS and α-spectrometry on the age determination of ivory

The reduced uncertainty of the ^{232}Th determination enabled a more reliable age determination of ivory. The dating was done by calculating the ratio of ^{228}Th/^{232}Th. Table 4.14 shows one example for the improved reliability of age determination of ivory. Comparing the results of the ^{228}Th/^{232}Th determinations based solely on α-spectrometry with those of the combined use of α-spectrometry and ICP-MS, the latter approach allowed for a clearly reduced uncertainty.

Table 4.14: Impact of the improved method on the age determination of sample No. 1.

	ICP-MS / α-spectrometry	**α-spectrometry**
a (^{228}Th) / mBq	2.1 ± 0.3	
a (^{232}Th) / mBq	0.13 ± 0.01	0.14 ± 0.06
^{228}Th/^{232}Th / a.u.	16 ± 2	15 ± 7
Calculated death of animal*	2005 ± 1	2004 ± 5
Actual death of animal	2005	

* Calculation was done by comparing the ratio of the activity concentration with a calibration curve, created by Schupfner and co-workers [3].

The mean values of the calculated ratios were almost equal. However, the uncertainty of the combined method was five times lower than the value when only α-spectrometry was used. As a consequence, the uncertainty of the age determination of the ivory sample was just one year (ICP-MS / α-spectrometry) instead of five years (only α-spectrometry). The comparison of the dating uncertainties of the samples No. 3 - 8 are shown in Table 4.15.

Table 4.15: Comparison of the dating accuracy of the newly developed technique with the old technique. Samples No. 3 - 8.

Sample No.	Dating result old method	Dating result new method
3	1998 ± 2	1999 ± 1
4	2004 ± 3	2003 ± 1
5	1999 ± 2	1998.2 ± 0.7
6	2006 ± 4	2006.0 ± 0.6
7	2002 ± 4	2002 ± 1
8	2003 ± 3	2003 ± 1

The dating results for the new and the old technique are according to the outcome obtained for sample No. 1. The mean value for the dating results for both techniques of the respective samples are equal or at least within the limits of the uncertainty. The uncertainties of the technique including ICP-MS measurements are significantly lower than the uncertainties for the technique with solely activity determination via α-spectrometry. Hence, an improvement of the dating accuracy can be achieved using the newly developed technique.

4.3.4 Conclusion

Experiments with standard solutions showed the possibility to combine two completely different techniques, namely, α-spectrometry and ICP-MS, for the reliable determination of ^{228}Th/^{232}Th. The application of the new method to ivory samples showed that the combination of ICP-MS and α-spectrometry is an attractive strategy to reduce the uncertainty of the determination of ^{232}Th as well as the uncertainty of the ratio ^{228}Th/^{232}Th. Thus, the new method contributes to an improved distinction of legal and illegal ivory, allowing for a more reliable determination of the age of ivory samples.

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4.4 Monitoring the time dependent equilibration of ^{228}Th and decay products in ivory via α-spectrometry

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Abstract

The worldwide population of elephants shows a rapid decline due to trafficking of ivory. Hence, a method is needed for the age determination to distinguish legal from illegal ivory. The analysis of ^{228}Th and ^{232}Th in ivory can be used for this purpose. This study provides a technique for the analysis of ^{228}Th in ivory. The thorium was extracted from ivory and measured after various time periods applying α-spectrometry until a secular radioactive equilibrium between ^{228}Th and its decay products was established. An equilibration period of 32 days was found. The uncertainty of the determination of the activity of ^{228}Th could be reduced by integrating the counts of the equilibrated decay products into the determination process.

4.4.1 Introduction

The total number of elephants in 2016 is assessed to roughly 350,000 animals in eighteen countries [1]. The rate of annual decline is eight percent [1], which accounts for roughly 28,000 animals. The reasons for this decline are the valuable ivory tusks of the elephants, which are sold on the black market. To prevent the elephant from extinction, the Convention on International Trade in Endangered Species of Wild Fauna and Flora was signed [2]. The Convention lists all specimen, which are protected since their entry in the appendices of the Convention. Therefore, the African Elephant (*Loxodonta Africana*) is protected since the year 1976 (in Germany) [2]. However, elephants are still poached, and a reliable method is needed for age determination of ivory to distinguish between legal (older than 1976) and illegal ivory for a successful criminal prosecution in Germany. Radionuclides are often used for age determination [3] in all kind of matrices, such as bones [4, 5], minerals [6, 7] and ivory [8, 9]. Schupfner and co-workers [9] investigated a method for ivory dating by analyzing the radionuclides ^{14}C, ^{90}Sr and the ratio of the activity concentrations of ^{228}Th and ^{232}Th. The combined analysis of these radionuclides allows for a correct and reliable age determination. The determination of the ratio of the activity concentrations of the thorium isotopes ^{228}Th and ^{232}Th in ivory via α-spectrometry is of interest for the age determination within the first 40 years after death of the animal [9]. The activity of ^{232}Th (about 0.04 mBq per g ivory ash [9]) can be considered constant due to the long half-life of the nuclide [10], whereas the activity of ^{228}Th changes after death of the elephant. The natural content of ^{228}Ra in ivory decays to ^{228}Th over ^{228}Ac [11]. Therefore, the activity of ^{228}Th rises in the first years after death of the elephant before reaching a maximum after roughly four years (about 1.7 mBq per g ivory ash [9]). After 40 years, which represent roughly seven half-lives of ^{228}Ra, the ^{228}Ra mostly vanished and the activity of ^{228}Th approximates that of ^{232}Th. Hence, the ratio of ^{228}Th and ^{232}Th decreases to a value of one [9]. Therefore, an analyzed ivory sample with a ratio of one is at least 40 years old. At this point, the activity of ^{228}Th is low (about 0.05 mBq per g ivory ash [9]) and the corresponding uncertainty of the determination is high. Thus, further investigations had to be carried out to reduce the uncertainty of the determination. The decay products of ^{228}Th, namely ^{224}Ra, ^{220}Rn, ^{216}Po, ^{212}Bi and ^{212}Po, which should be in a secular radioactive equilibrium with ^{228}Th after some time, could be used to overcome the drawback of increased uncertainty. The equilibrium or dis-equilibrium between radionuclides and their decay products in various kinds of ecological systems is well described in the literature [12]. Campana and co-workers [13] used the dis-equilibrium of $^{210}Pb/^{226}Ra$ and $^{228}Th/^{228}Ra$ for the age determination of fish. Since the parameters of the radioactive decay of ^{228}Th and the above-mentioned decay products are well known [14], the expected count ratios after equilibration can be predicted.

The scope of this study was to demonstrate that a secular radioactive equilibrium of ^{228}Th and its decay products was formed after a certain period of time. It was shown that the counts of the α-particles of the decay products of ^{228}Th could be used to reduce the uncertainty of the activity determination of ^{228}Th. The thorium (Th^{4+}) was extracted from ivory and measured after several time periods. The equilibration was monitored and its progress was indicated by the changing ratio of the decay product counts versus the ^{228}Th counts. After a sufficient amount of time, the equilibration of ^{228}Th and its decay products took place and all counts could be used for an improved determination of ^{228}Th in ivory.

4.4.2 Experimental

All used chemicals were analytical grade and the substances were used without further purification. Concentrated sulfuric acid, concentrated hydrochloric acid and concentrated ammonia solution were purchased from VWR (Ismaning, Germany). TEVA® resin was purchased from Triskem International (Bruz, France). Aluminum nitrate nonahydrate, concentrated nitric acid and trioctylphosphine oxide were purchased from Merck (Darmstadt, Germany). Chromosorb® W-AW-DMCS (80-100 mesh) was purchased from CS-Chromatographie Service GmbH (Langerwehe, Germany). The analyzed ivory sample was provided by the zoological garden in Wuppertal (extraction from the living elephant in January 2016, Code 207, Germany). The amount of ivory ash used for the sample preparation was 8.7 g. The α-spectrometric measurements were carried out with ion implanted silicon detectors in an Octête α-chamber model U-034-1200-AS from EG&G Ortec (Meerbusch, Germany) with a detector surface of 240 mm^2, which was controlled by the software Gamma Vision 5.1. All α-measurements took place in the same chamber with the same detector. The instruments, chemicals and methods for sample preparation of ivory were already described in the literature [5]. The procedure is shortly summarized in this paragraph. The raw ivory was dried, crushed and incinerated in an oxygen stream at 650°C. The inorganic remains were milled, dissolved in concentrated nitric acid to remove remaining organic compounds and fumed down to dryness. This procedure was repeated with concentrated hydrochloric acid. The remaining ivory ash was dissolved in 3 M HNO_3 / 1 M $Al(NO_3)_3$ solution and used for two consecutive solid phase extraction procedures [5]. The column material for the first solid phase extraction was trioctylphosphine oxide impregnated on Chromosorb® and the column material for the second solid phase extraction was TEVA® resin. The eluate was free of ivory matrix, which mainly consists of calcium phosphate, and was used for electrodeposition on a stainless-steel chip (Ø = 2 cm, Ø of deposition surface = 1.5 cm). A removal of the matrix was crucial for a successful electrodeposition procedure and a good α-measurement. A deposited layer of calcium phosphate on the steel chip would lead to self-adsorption of α-particles and poor signals for the α-measurement. The sample preparation was done within one day. The chip was measured four times after various time periods via α-spectrometry. The parameters of the measurements are shown in Table 4.16. The chemical yield of the analysis was calculated via isotope dilution analysis.

Table 4.16: Parameters of the detection of α-particles applying α-spectrometry.

Measurement No.	Passed time since sample preparation / d	Measuring time / s
1	7	350,000
2	32	530,000
3	63	270,000
4	417	790,000

Distance of sample and detector surface was 5 mm. Limit of detection for the measurement of ^{228}Th was 0.2 mBq, which was far lower than the measured ^{228}Th activity in the ivory sample (value is given in the next chapter). The background of the detector was observed prior to the sample measurements until no recoil signals were detectable anymore. Several background measurements were done with measuring times between 750,000 – 2,000,000 s. The received counting rates for the respective energy ranges were used to calculate the expected value of the background counts during the sample measurement. The energy calibration was done with a steel chip with electrodeposited ^{239}Pu, ^{241}Am and ^{244}Cm (5.157 MeV, 5.486 MeV and 5.805 MeV [10]) as calibration supplement. The measurement time was 2,000 s. The signal maxima of the three calibration radionuclides were used for a linear energy calibration. The energies were assigned to the channels. The peaks of the sample measurements were identified according to the energy values of the radionuclides described in [10].

Since the evaluation of the α-spectra was crucial in this study, the used equations are described. The counts of the radionuclides were evaluated by determination of the count peak area. The ratios of the nuclides versus ^{228}Th were calculated by dividing the count peak areas of the respective decay products by the count peak area of ^{228}Th. Equation 17 shows the determination of the activity of ^{228}Th (A_{228Th}) without including the counts of the decay products.

$$A_{228Th} = \frac{\frac{(N'_{228Th} - N_{0228Th})}{t_L}}{\eta_{phy} \cdot \eta_{chem} \cdot Y_{228Th}} \tag{17}$$

N'_{228Th} are the gross counts of the α-peak of ^{228}Th, N_{0228Th} is the expected value of the background counts of ^{228}Th, t_L is the lifetime, η_{phy} is the counting efficiency (0.241 ± 0.002 counts / (s·Bq)), η_{chem} is the chemical yield (60%) of the sample preparation and Y_{228Th} is the emission probability of ^{228}Th. Equation 18 shows the uncertainty $u(A_{228Th})$ of the activity of ^{228}Th calculated by Equation 17.

$$u(A_{228Th}) = A_{228Th} \cdot \frac{\sqrt{\sqrt{N'_{228Th}}^2 + \sqrt{N_{0228Th}}^2}}{N'_{228Th} - N_{0228Th}} \tag{18}$$

After the establishment of the equilibration of ^{228}Th and its decay products, the counts of the decay products were used for the determination of the activity and the corresponding uncertainty of ^{228}Th. This is achieved by substituting all values in Equation 17 and Equation 18, which are designated to ^{228}Th, by the sums of the respective values of all evaluated nuclides e.g. N'_{228Th} is substituted by $\Sigma N'_i$, whereas i represents ^{228}Th, ^{224}Ra, ^{220}Rn, ^{216}Po and ^{212}Bi.

4.4.3 Result and discussion

Some requirements needed to be fulfilled for the study of the equilibration of ^{228}Th and its decay products. The sample preparation had to ensure that the separation of thorium from other radionuclides, especially the decay products of ^{228}Th, was selective. Otherwise the radionuclides, which were electrodeposited and not formed by the decay series would falsify the result. This was ensured by using two successive solid phase extraction procedures. The trioctylphosphine oxide impregnated on Chromosorb® separated the thorium from the ivory matrix and the highly specific TEVA® resin ensured a selective thorium separation from disturbing radionuclides [15]. Moreover, the ion implanted silicon detectors had to be free of impurities from previously measured samples and not yet decayed recoil nuclei [16]. Therefore, in advance to each measurement the background spectrum was observed until all short-lived disturbing radionuclides, located at the inner walls of the α-chamber decayed. Since the ^{232}Th series is well described in the literature [17], a prediction about the expected α-spectrum and the relative ratios of ^{228}Th and the decay products after equilibration could be made. Table 4.17 shows the details about all evaluated alpha emitting radionuclides in the ^{232}Th series.

Table 4.17: Details about the radionuclides and their decay energies, which were evaluated in this study [10].

Nuclide	**Evaluated decay energies / keV**	**Emission probability / $(Bqs)^{-1}$**	**Half-life**	**Expected ratio versus ^{228}Th**
^{228}Th	5340, 5423	0.9942	1.9 a	-
^{224}Ra	5685, 5449	0.9998	3.7 d	1
^{220}Rn	6288	0.9989	56 s	1
^{216}Po	6778	1.000	0.15 s	1
^{212}Bi	6051, 6090	0.9703 (0.6406) [a]	60.6 min	0.35
^{212}Po	8785	1.000	0.3 µs	0.41

[a] ^{212}Bi undergoes a branching with 36% α-decay, the value in brackets is the emission probability for the 64% β-decay.

After equilibration, the ratio of the decay products ^{224}Ra, ^{220}Rn and ^{216}Po should be one (ratio of the respective counts versus ^{228}Th). As these nuclides show emission probabilities of one and no branching, it can be assumed that each ^{228}Th nucleus decays to ^{224}Ra, ^{220}Rn,^{216}Po and ^{212} Bi, respectively, resulting in a ratio of one for the net count areas of the first three decay products. ^{212}Bi should have the ratio 0.35 since it has a branching for the alpha decay of 36% and an emission probability of 0.9703. ^{212}Po is the product of the ^{212}Bi β-decay with a branching of 64% and an emission probability of 0.6406 (compare Table 4.16). Considering (multiplying) these two values an expected ratio versus ^{228}Th of 0.41 for the ^{212}Po counts can be assumed.

At this point some losses of decay products should be considered as well. There is a possibility for each decaying nuclide that the resulting force of the decay removes the respective decay product from the steel chip leading to a removal from the α-chamber due to the applied vacuum. This recoil nucleus is no longer available for the detection of its decay products. This results in a theoretical decrease of the counts of the decay products. Furthermore, the rare gas radon is formed during the decay chain. Although its half-life is just 56 seconds, it could be possible that the emanation of ^{220}Rn is taking place [18]. This would result in a counts loss for all decay products of ^{220}Rn. Hence, this possible artifact was under particular observation during evaluation.

Once the sample preparation was done, the measurements were carried out with the same steel chip after different time periods. Fig 4.8 shows an α-spectrum seven days after electrodeposition of the thorium and Fig 4.9 shows an α-spectrum which was measured 32 days after the electrodeposition.

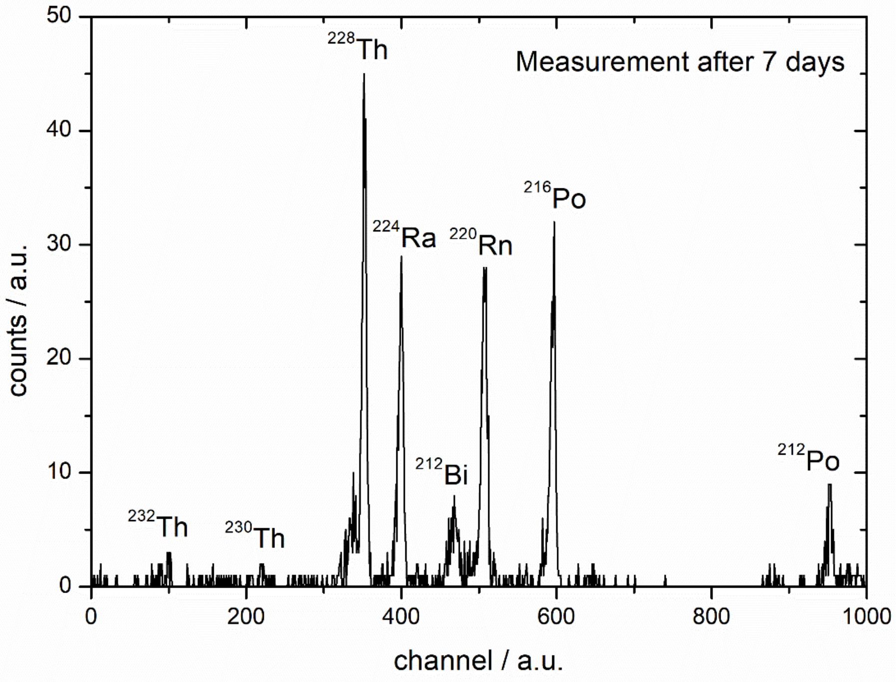

Figure 4.8: α-spectrum of the purified thorium on the steel chip seven days after electrodeposition. Measurement time: 350,000 s, Distance of detector and sample: 5 mm.

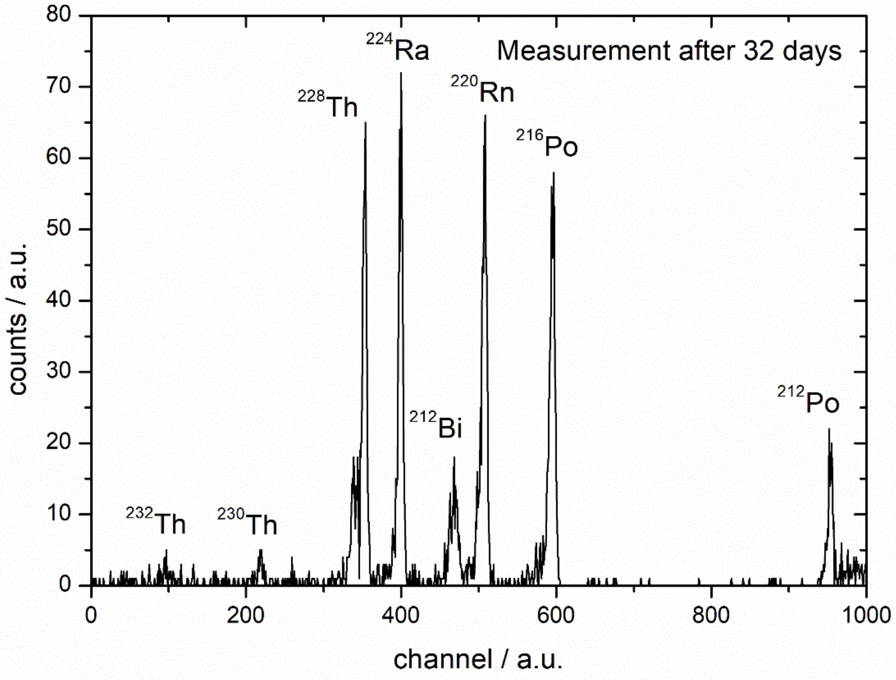

Figure 4.9: α-spectrum of the purified thorium on the steel chip 32 days after electrodeposition. Measurement time: 530,000 s, Distance of detector and sample: 5 mm.

Figure 4.8 shows the alpha spectrum seven days after the sample preparation and the electrodeposition. It shows a not yet achieved secular radioactive equilibrium, whereas Figure 4.9 shows the alpha spectrum after 32 days with an advanced state of secular radioactive equilibrium, since the peak ratios approximate the expected values as can be seen in Table 4.17. In general, the spectra show that the sample preparation and the removal of disturbing radionuclides, such as ^{241}Am, ^{244}Pu and ^{238}U, was successful, since no additional α-peaks were visible, besides the α-peaks of ^{232}Th, ^{230}Th, ^{228}Th and the α-peaks of the decay products of ^{228}Th. After seven days, the secular radioactive equilibrium was not yet reached because the ^{228}Th α-peak was significantly larger than the α-peaks of the decay products. The secular radioactive equilibrium was achieved after 32 days since the expected ratios of the decay products versus ^{228}Th matched well with the measurement outcome, except for ^{212}Po. The ratios of the decay products versus ^{228}Th for all measurements are shown in Table 4.18.

Table 4.18: Calculated ratios of the decay products versus ^{228}Th after different time periods.

Time period / d	**Ratio versus ^{228}Th**				
	^{224}Ra	**^{220}Rn**	**^{216}Po**	**^{212}Bi**	**^{212}Po**
7	0.68	0.79	0.71	0.25	0.22
32	0.99	1.01	0.98	0.34	0.32
63	1.00	1.01	1.01	0.34	0.31
417	0.99	1.01	0.99	0.35	0.34
Expected ratios*	1	1	1	0.35	0.41

*after equilibration

The measurements showed that after some time the ratios increased and approached the expected values described in Table 4.17. Hence, an equilibration of ^{228}Th and its decay products occurred after roughly one month. That was not the case for ^{212}Po, whose counts were too low for the expected ratio. It was assumed that the reason for this was the fact that ^{212}Po is the last part of the decay chain and that its equilibration lasts longer. An additional measurement was done after roughly one year, but the result concerning the formation of the ratio could only be improved slightly. Another explanation for the low ^{212}Po ratio could be that the counting efficiency becomes worse for higher energies due to different interactions of high energetic α-particles with the detector material. Thus, the ^{212}Po counts were too low. More investigations are necessary to verify the reason for this disagreement. Besides ^{212}Po, no significant count loss due to recoil nuclei and the emanation of ^{220}Rn could be found. After the equilibrium was achieved, it was possible to use the counts of the decay products (without ^{212}Po) to reduce the uncertainty of the determination of the activity of ^{228}Th.

Using the sum of all counts of all equilibrated nuclides (Equation 1 and Equation 2), an activity for ^{228}Th of (6.2 ± 0.1) mBq could be calculated, compared to an evaluation solely with the α-peak of ^{228}Th, which resulted in a value of (6.2 ± 0.3) mBq. These values count for the measurement in Figure 4.8. The value for the activity itself remained equal but the uncertainty for the activity determination with the presented calculation technique could be reduced by 67%. Nevertheless, a validation of this technique with more samples of different ages needs to be done. The technique should work for all samples. A promising impact on the uncertainty determination for samples with an age up to 40 years can be expected. For these samples, the ^{228}Th activity is low and the low signal in the α-spectrometry results in a high uncertainty. This high uncertainty can be reduced using the presented technique.

4.4.4 Conclusion

It was shown that ^{228}Th, which was extracted from ivory, underwent an equilibration after deposition on a steel chip after 32 days. The expected ratios of the counts of the decay products versus the counts of ^{228}Th were achieved after about one month, except for ^{212}Po. This enables the inclusion of the decay products for the determination of ^{228}Th. The uncertainty of the determination could be decreased by 67% in contrast to an evaluation with the solely ^{228}Th counts.

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4.5 Development of a method for yield determination of radioanalytical analysis via ICP-MS

4.5.1 Introduction

The demand for radiometric analysis is high. The knowledge of the activity concentrations of various relevant isotopes is of interest for the monitoring of the environment [1], industrial facilities [2] and nuclear facilities [3]. The Radiation Protection Ordinance [4] regulates the limits of the allowed isotope activity concentrations in waste material. Since the limits are very low for some isotopes [4], it is a challenge to perform the analysis of isotopes in the low ppb or ppt concentration range [5]. Dependent on the matrix of the samples, which can be modest (water [6]) as well as complex (concrete [7] or ivory [8]), the analysis must be done with highly specific extraction [9] and enrichment techniques. Even then the analysis is difficult for low concentrated isotopes. Many radiometric detection techniques, such as the α-spectrometry [10] demand a matrix free measurement supplement with enough yield. The yield of radiometric analysis can be determined effectively and effortlessly via the isotope dilution method [11]. An isotope (yield tracer) of the target analyte is added with known activity to the sample at the beginning of the analysis. In the best case it is an artificial isotope that is not contained in the environment and thus in the sample, such as ^{227}Th or ^{229}Th for the analyte ^{232}Th or ^{235}U for the analyte ^{238}U. The tracer undergoes the same losses during the sample preparation as the target analyte and with the contemporaneous measurement of both isotopes the remaining activity of the tracer and thus the yield can be determined. This technique is widely used for radioanalytical analysis of all kind of samples [12] and target analytes [13]. The use of a radioactive tracer is dependent on the availability, the target analytes and the handling permission of the laboratory. The addition of a radioactive tracer for the analysis of a non-radioactive sample causes bureaucratic efforts, increased safety precautions and the associated costs. Hence, avoiding the use of a radioactive tracer would be a great gain for the general terms of a radio analysis. Otherwise, a low-level radio analysis, such as the age determination of ivory [14] would be treated as an active analysis according to the Radiation Protection Ordinance. It seems obvious to substitute the isotope dilution method by a technique that preserves the inactive character of the sample and the procedure. This technique must have low limits of detection and must be suitable to measure isotopes, which would be the main target in this context. The inductively coupled plasma mass spectrometry (ICP-MS) is widely used in the field of ion and elemental analysis [15] in all kind of samples [16, 17] with very low detection limits [18]. The ICP-MS is well established in the field of radio analysis for the determination of various isotopes, such as $^{135/137}$Cs [19] or uranium and plutonium isotopes [20]. The ICP-MS is already used for the determination of ^{232}Th for the purpose of age determination of ivory [21] and thus suitable for an extended application for yield determination in the context of ivory dating.

The scope of this study was the development of a technique for the inactive yield determination of low-level environmental or industrial samples. For this purpose, the ICP-MS was integrated into the normal process of a radio analysis. The focus was on an effortless but effective integration of the ICP-MS measurement. The technique was first developed for a simple and initially salt free matrix, namely aerosol filter. Then, the technique was adjusted for the use of yield determination in the context of the age determination of ivory, where drawbacks caused by the sample matrix had to be overcome. A yield determination strategy for the isotope analysis of ^{238}U in aerosol filter and ^{232}Th in ivory was found.

4.5.2 Experimental

The purity of the used chemicals was p.a. grade and the substances were used without further purification. Concentrated sulfuric acid, concentrated hydrofluoric acid, concentrated hydrochloric acid and concentrated ammonia were purchased from VWR (Ismaning, Germany). Chromosorb® W-AW-DMCS was purchased from CS-Chromatographie Service GmbH (Langerwehe, Germany). UTEVA® resin and TEVA® resin were purchased from Triskem International (Bruz, France). The thorium (1 ppm) and bismuth (1 ppm) standard solutions were purchased from Spetec (Erding, Germany). Ultrapure concentrated nitric acid, concentrated nitric acid, uranium standard solution (1 ppm), aluminum nitrate nonahydrate and trioctylphosphine oxide were purchased from Merck (Darmstadt, Germany). The experiment with ivory was done with 4.05 g ivory ash (Code BfN 7).

The uranium analysis in aerosol filter is described in the following. The filter was dried at 500°C over night. The filters were dissolved in a mixture of concentrated hydrofluoric acid and concentrated nitric acid (1:1). The solution was fumed down to dryness and treated three times with concentrated nitric acid to remove traces of hydrofluoric acid. The inorganic residue was dissolved in 3 M HNO_3 and a solid phase extraction procedure with UTEVA® resin was done. The uranium was separated from disturbing radionuclides. The eluent was free of matrix and the uranium was electrodeposited onto a stainless-steel chip for an α-spectrometric measurement. After the measurement, the uranium was detached from the steel chip by heating the chip with 100 µL of concentrated nitric acid on the surface of the deposition area. For ICP-MS measurements, 50 µL of sample was taken from the sample solution prior to the UTEVA® separation step and from the solution after the detachment of the uranium from the steel plate. 10 ppb of thorium standard were added as internal standard and the solutions were filled up to 10 mL with 1% HNO_3 solution.

The procedure of the thorium analysis in ivory and the ICP-MS operation parameters are already described in the literature [21]. The ICP-MS measurements of the thorium in the ivory were done as follows. The eluates of the trioctylphosphine oxide (TOPO) and the TEVA® solid phase extraction procedures were fumed down to dryness, the residue was dissolved in 1% HNO_3, 10 ppb of bismuth standard was added as internal standard and the solutions were filled up to 10 mL with 1% HNO_3 solution. Additionally, 100 mg of ivory ash were dissolved in 50 mL 1% HNO_3 and 10 ppb of bismuth standard was added as internal standard. The solutions were filtered using an 0.45 µm syringe filter prior to the measurements.

4.5.3 Result and discussion

Universal strategy for yield determination of radioanalytical analysis of long-lived nuclides via ICP-MS

The analyte losses during sample preparation could be determined by two comparative measurements. The first measurement gives the initial analyte concentration and serves as absolute value. This sample was drawn from the dissolved original sample prior any sample preparation procedures. The measured analyte content represented 100%. The second sample for ICP-MS measurement was drawn after the α-measurement. To do so, the deposited analyte must be removed from the steel chip via heat and concentrated nitric acid. The content in the received volume represented the remaining analyte after sample preparation and the ratio of both ICP-MS measurement results was equal to the chemical yield of the analysis. This strategy was used for the uranium determination in aerosol filter. Table 4.19 shows an overview over the relevant data for the chemical yield determination of this analysis.

Table 4.19: Relevant data of the ICP-MS measurement for yield determination of the uranium determination in aerosol filter. Used solution for sample preparation was 9.82 g. Internal standard was 10 ppb ^{232}Th. Volume for measuring solution was 10 mL and the solvent was 1% HNO_3.

	Mass of overall solution / g	**Mass of solution for ICP-MS / g**	**Calculated concentration of ^{238}U / ppb**
Before analysis	20.03	0.219	61.9
After α-measurement	12.47	0.222	45.8

Considering all dilution factors and the fact that only 9.82 g of the digestion solution was used for the analysis an overall chemical yield for all sample preparation steps of 94% was calculated. The calculated chemical yield for this simple matrix seemed convenient compared to former experiences with this analysis and a contamination of ^{238}U during the analysis, which would pretend a high yield was excluded, since ^{238}U is not omnipresent in the nature. Thus, the described procedure was chosen for the determination of the chemical yield in radioanalytical analysis.

Application of the developed strategy for yield determination on the analysis of ^{228}Th/^{232}Th in ivory

The yield determination strategy, which is described above was applied to the ^{228}Th/^{232}Th analysis in ivory. The target analytes in this analysis were the isotopes ^{228}Th and ^{232}Th. Since both isotopes are associated with the same element, it was assumed that ^{228}Th and ^{232}Th were affected in a similar way by the sample preparation procedure and they underwent the same losses. ^{232}Th was chosen as yield indicator, which could be measured via ICP-MS. ^{232}Th is present in sufficient concentration in ivory for the ICP-MS measurement, whereas ^{228}Th has a very low concentration [21]. First, the strategy developed for aerosol filters was applied. Additionally, the well-known technique of isotope dilution analysis for yield determination was conducted to validate the results from the new yield determination technique via ICP-MS. Unfortunately, two drawbacks had to be overcome. The initial measurement for the 100% value was strongly interfered by the high salt content caused by the ivory matrix. An unnatural high ^{232}Th concentration was calculated leading to a yield lower than 5%, which could not be verified by the result of the isotope dilution technique (96%). Thus, the initial measurement for the 100% value was made after the first solid phase extraction step with trioctylphosphine oxide. The second drawback was the fact that thorium hydroxide deposited on the steel chip could not properly be detached by the standard procedure. Hence, the ICP-MS measurement for the second measurement was made directly before the electrodeposition step, when the thorium was still in solution. The electrodeposition was done for two hours, which enables the assumption of a quantitative deposition of the thorium on the steel chip. The results of both ICP-MS measurements and the calculated chemical yield are shown in Table 4.20. The chemical yield calculated by the isotope dilution analysis is given as well.

Table 4.20: Result for the modified yield determination strategy by ICP-MS for the thorium analysis in ivory. The calculated chemical yield by the isotope dilution analysis is given for comparison. Limit of detection for the isotope ^{232}Th for ICP-MS was 55 ppt.

	Measuring volume / mL	**^{232}Th concentration / ppb**
After TOPO	10	1.23
Prior to electrodeposition	10	1.17
Yield determination by ICP-MS	96%	
Yield determination by isotope dilution analysis	96%	

The calculated chemical yields for the newly introduced technique by ICP-MS and the common isotope dilution technique matched very well. The good accordance of the results showed that the common isotope dilution technique can be substituted by a yield determination via ICP-MS. This would significantly lower the costs for the analysis, since the handled activities would be lower than any limits in the Radiation Protection Ordinance. That would significantly reduce the financial and bureaucratic efforts, which would be necessary for this analysis otherwise.

Since the technique was applied only once on the thorium analysis in ivory, it needs to be noted that the experiment needs to be repeated several times for a further validation. Furthermore, the analyte loss by the first solid phase extraction procedure (TOPO) was neglected. However, the determination of the ^{228}Th/^{232}Th ratio in ivory is done to determine the age of the ivory. Since a ratio is calculated here, the exact value of the chemical yield is not crucial. The ratio remains equal, independent of the chemical yield. It only has to be ensured that the analyte is not completely lost and that measured low activities for ^{232}Th and ^{228}Th are caused by the high age of the ivory. The presented technique is suitable for this special objective.

4.5.4 Conclusion

The technique for yield determination for the analysis of ^{238}U in an aerosol filter showed a convenient result and thus could be used as substitution for the common isotope dilution analysis. The technique was applied in a modified form to the thorium analysis in ivory. A comparison with the isotope dilution analysis, which was carried out in parallel, showed that the yield determination with ICP-MS obtained similar results. Thus, the common isotope dilution technique could be replaced by ICP-MS measurements, which were integrated in the procedure of the sample preparation. The inactive character of the ivory analysis could be preserved, which significantly reduces the costs and the effort for radiation protection.

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5. Summary

In this work, the significance of the determination of the ratio of the activity concentrations of ^{228}Th and ^{232}Th in the context of age determination of ivory was discussed and the corresponding dating uncertainty was reduced. Calibration curves for the relevant isotopes for ivory dating, namely ^{14}C, ^{90}Sr and ^{228}Th/^{232}Th, were created by analyzing young ivory samples with known age. It was shown that the age determination of ivory via the thorium isotopes will become an indispensable and powerful technique in the future. The applicability of the bomb curve dating via the isotopes ^{14}C and ^{90}Sr will fade, due to ambitious findings for ivory, which will be poached within the future. Since the ratio ^{228}Th/^{232}Th is not affected by the atomic bomb tests in the sixties, unlike the isotopes ^{14}C an ^{90}Sr, the age determination via ^{228}Th/^{232}Th will also work in the future and the method will be able to identify illegal ivory, which is not older than 40 years.

The validation of the created time-depending calibration curve of ^{228}Th/^{232}Th in ivory was done by repeated analysis of the same ivory samples with known age after half a year and by repeated analysis of an ivory sample within two years. The expected trend of the ratio change could be confirmed by these experiments. The activity concentration ratio ^{228}Th/^{232}Th rises after death of the elephant, reaches a maximum after roughly four years, decreases and assimilates to a value of one after 40 years.

The uncertainty of the overall ^{228}Th/^{232}Th determination could be reduced by developing improved strategies for the determination of the ^{228}Th and ^{232}Th activities. ^{232}Th showed low counting rates and high uncertainties for the determination via α-spectrometry, but ^{232}Th was well accessible via inductively coupled plasma mass spectrometry (ICP-MS). An ICP-MS measurement was integrated in the common analytical procedure. The approach was validated by the analysis of ^{232}Th standard solutions as well as ivory samples. It was shown that the ICP-MS and the α-spectrometry provided similar results. The benefit of the improved technique was the significant lower uncertainty of the ^{232}Th determination by ICP-MS compared to α-spectrometry. The evaluation of a representative ivory sample showed that the uncertainty could be reduced to a value down to 17% of the uncertainty of the ^{232}Th determination by α-spectrometry. This was reflected in an improved dating uncertainty of one year, instead of five years in this case.

The determination of the ^{228}Th activity could be improved by evaluating the signals of the decay products of ^{228}Th via α-spectrometry. After extraction of thorium from the ivory matrix, the decay series ^{228}Th, ^{224}Ra, ^{220}Rn, ^{216}Po and ^{212}Bi established a secular radioactive equilibrium. The formation of the secular radioactive equilibrium could be monitored by repeated measurements of the same extracted thorium after time periods. The signal ratios of these isotopes versus ^{228}Th after an achieved equilibrium could be predicted and experimentally validated. A time period of 32 days for the establishment of the secular radioactive equilibrium was found. By using the signals of the decay products for the determination of the ^{228}Th activity, the uncertainty of the former ^{228}Th determination method could be reduced to a value down to 33% of the uncertainty of the evaluation without the decay products of ^{228}Th.

The ICP-MS was applied for yield determination for the thorium extraction from ivory. The strategy was developed for a simple matrix and applied to an ivory sample. Two ICP-MS measurements were made during the analytical procedure. One measurement was made after the matrix removal via a trioctlyphosphine oxide solid phase extraction procedure and one measurement was made prior to the electrodeposition of the thorium on a steel chip. The yield result matched well with the result provided by the common isotope dilution yield determination method. The substitution of the isotope dilution method, and the associated prevented addition of external activity in form of a yield tracer, with the yield determination via ICP-MS enables the benefit of an inactive analysis.

6. Zusammenfassung in deutscher Sprache

Im Zuge dieser Arbeit wurde die Bestimmung des Aktivitäten Verhältnisses von ^{228}Th und ^{232}Th zum Zwecke der Altersdatierung von Elfenbein weiterentwickelt. Die Bedeutung der Methode wurde diskutiert und deren Datierungsunsicherheit reduziert. Es wurden Kalibrierkurven für die datierungsrelevanten Isotope ^{14}C, ^{90}Sr und ^{228}Th/^{232}Th erstellt, indem junge Elfenbeinproben bekannten Alters analysiert wurden. Dadurch konnte die Datierungsstrategie für Elfenbein durch diese Isotope und deren Anwendbarkeit diskutiert werden. Es wurde aufgezeigt, dass die Altersbestimmung von Elfenbein durch die Thorium-Isotope eine unverzichtbare und bedeutende Methode in der Zukunft sein wird. Die Bedeutung der ^{14}C- und ^{90}Sr-Analyse und deren Einsatz für die Elfenbeindatierung wird schwinden, da deren Analyse uneindeutige Ergebnisse für künftig gewildertes Elfenbein zeigen wird. Das Verhältnis ^{228}Th/^{232}Th wird, anders als die Isotope ^{14}C und ^{90}Sr, nicht von den Atombombentests in den sechziger Jahren beeinflusst und daher wird die Datierung mittels ^{228}Th/^{232}Th auch in der Zukunft in der Lage sein, illegales Elfenbein zu identifizieren, das nicht älter als vierzig Jahre ist.

Die Validierung der erstellten zeitabhängigen Kalibrierkurve von ^{228}Th/^{232}Th in Elfenbein wurde durch wiederholte Analysen derselben Elfenbeinproben nach einem halben Jahr und in einem Fall durch die wiederholten Analysen einer Probe über einen Zeitraum von zwei Jahren durchgeführt. Der zu erwartende Trend des Verhältnisses ^{228}Th/^{232}Th konnte durch die gemachten Experimente bestätigt werden. Das Verhältnis ^{228}Th/^{232}Th in Elfenbein steigt direkt nach dem Tod des Elefanten an und erreicht nach etwa vier Jahren ein Maximum. Ab diesem Zeitpunkt fällt das Verhältnis ab und nähert sich nach 40 Jahren einem Wert von eins an.

Die Gesamtunsicherheit der ^{228}Th/^{232}Th-Bestimmung konnte durch verbesserte Methoden zur Bestimmung der Aktivitäten von ^{228}Th und ^{232}Th verringert werden. ^{232}Th zeigte niedrige Zählraten und hohe Unsicherheiten bei α-spektrometrischen Messungen, wohingegen ^{232}Th jedoch gut mittels Massenspektrometrie mit induktiv gekoppeltem Plasma (ICP-MS) messbar war. Eine ICP-MS-Messung wurde in die bisherige analytische Durchführung integriert. Die Strategie wurde anhand der Analysen von Standardlösungen validiert und auf Elfenbeinproben übertragen. Beide Bestimmungsmethoden wurden auf die gleichen Elenbeinproben angewandt. Die Ergebnisse beider Methoden stimmten überein. Der Vorteil der integrierten ICP-MS-Bestimmung lag in der deutlich verringerten Unsicherheit der ^{232}Th-Bestimmung im Vergleich zu der Bestimmung mittels α-Spektrometrie. Bei der Analyse einer repräsentativen Elfenbeinprobe erreichte die Unsicherheit der ^{232}Th-Bestimmung durch ICP-MS einen Wert, der 17% des Wertes der α-Spektrometrie entsprach. In diesem Fall entsprach das einer Verbesserung des Datierungsergebnisses auf eine Unsicherheit von einem Jahr anstatt von fünf Jahren.

Die Unsicherheit der Bestimmung von ^{228}Th wurde verringert, indem die Signale der Zerfallsprodukte des Isotops ^{228}Th mit in die Auswertung der α-Spektrometrie einbezogen wurden. Nachdem Thorium aus der Elfenbeinmatrix extrahiert wurde, stellte sich ein säkulares Gleichgewicht der Zerfallsreihe bestehend aus ^{228}Th, ^{224}Ra, ^{220}Rn, ^{216}Po und ^{212}Bi ein. Die zeitliche Einstellung des Gleichgewichts wurde anhand wiederholter Messungen desselben Thorium-Präparates über einen längeren Zeitraum verfolgt. Die zu erwartenden Verhältnisse der Signale der Zerfallsprodukte zu ^{228}Th nach dem Erreichen des Gleichgewichts wurden theoretisch berechnet und durch die erhaltenen Ergebnisse bestätigt. Die Dauer zur Einstellung des Gleichgewichtes betrug 32 Tage. Durch die Einbindung der Signale der Zerfallsprodukte in den Bestimmungsprozess der Aktivität von ^{228}Th, konnte dessen Aktivitätsunsicherheit auf einen Wert reduziert werden, der 33% der Unsicherheit der alten Methode entsprach.

Die ICP-MS wurde zur Bestimmung der chemischen Ausbeute der Extraktion von Thorium aus Elfenbein angewandt. Die Methode wurde anhand eines einfachen Matrixsystems entwickelt und in modifizierter Form auf Elfenbein übertragen. Dazu waren zwei ICP-MS-Messungen im Laufe der Analyse erforderlich. Eine Messung wurde gemacht, nachdem die Matrix durch eine Festphasenextraktion mittels Trioctylphosphinoxid entfernt wurde. Die zweite Messung erfolgte direkt vor der Elektroplattierung des Thoriums auf einem Stahlplättchen. Der Vergleich beider Messergebnisse lieferte die chemische Ausbeute der Extraktion. Das Ergebnis der neu entwickelten Methode entsprach dem Ergebnis der gängigen Isotopenverdünnungsanalyse. Der Ersatz der Isotopenverdünnungsanalyse durch die entwickelte Ausbeutenbestimmung durch ICP-MS und die dadurch vermiedene Zugabe eines radioaktiven Ausbeutentracers ermöglichte es, die Analyse zur Datierung von Elfenbein als inaktiv zu klassifizieren.

Erklärung

Ich habe die vorliegende Arbeit selbstständig verfasst, keine anderen als die angegebenen Quellen und Hilfsmittel benutzt und bisher keiner anderen Prüfungsbehörde vorgelegt. Von den in §27 Abs. 5 vorgesehenen Rechtsfolge habe ich Kenntnis genommen.

Regensburg, den 03.07.2019

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(Andreas Schmidberger)