

**2<sup>nd</sup> Progress Report of the R+D-project:  
„Age determination of ivory and other parts of animals, e.g. rhino, coat  
and tortoiseshell“  
Subproject: „Age determination“  
FZK: 3510 86 0100**

The certainty of dating ivory shall be increased by determination of its isotope signature (fingerprint). This isotope signature consists of the radionuclides  $^{14}\text{C}$ ,  $^{90}\text{Sr}$ ,  $^{232}\text{Th}$  and  $^{228}\text{Th}$  which must be analyzed in the ivory matrix. A coupled analysis method shall be developed which is efficient, sensitive and precise for analyzing the above-named radionuclides. The validation of this method shall be accomplished by the use of certified standard materials. Furthermore it shall be proofed, if the age determination is suitable for other animal tissue. The time period of this report is from January, 11<sup>th</sup> to July, 10<sup>th</sup> in 2011 and includes following steps:

- Investigations if the separation of potassium-40 ( $^{40}\text{K}$ ) is successful.  $^{40}\text{K}$  is the most important contaminant within the  $^{90}\text{Sr}$  analysis. A complete decontamination of  $^{40}\text{K}$  ensures that the measured count rates of a  $^{90}\text{Sr}$  analysis are only derived from  $^{90}\text{Sr}$  and background effects
- The validation of the coupled analysis method is started with proper certified standards. The results can be compared to the certified values and so the accuracy of the coupled analysis method can be evaluated.
- Some prearrangements are made to analyse the isotope signature in different parts of one tusk to prepare a distribution curve with these data. The tusk, which was fetched in Montabaur in December 2010, was cut in different pieces suited for our purpose.

All work described was done by Stefanie Schmied (Sample work-up, analysis of  $^{90}\text{Sr}$ ) and Matthias Brunnermeier (analysis of  $^{14}\text{C}$ ,  $^{228}\text{Th}$  and  $^{232}\text{Th}$ ). Material expenses were spent according to the approval. All measurements were carried out as services in own account. This includes different low-level radiation measurement systems provided by the URA-Laboratory and an ICP-OES system provided by the Center of Chemical Analysis of the department of chemistry/pharmacy.

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## 1. Separation of $^{40}\text{K}$ from the $^{90}\text{Sr}$ -measuring compound

### 1.1 Introduction

The most important, naturally occurring radionuclide which interferes the determination of  $^{90}\text{Sr}$  is  $^{40}\text{K}$ . Naturally occurring potassium consists of 0,012%  $^{40}\text{K}$ , which is a radioactive isotope. It has a half-life of about  $1,28 \cdot 10^9$  years and decays to stable  $^{40}\text{Ca}$  by emitting  $\beta^-$ -radiation amongst others. It is very important that the  $^{90}\text{Sr}$ -measuring compounds are free of potassium because the ionizing radiation of  $^{40}\text{K}$  would increase the count rate and the results for the  $^{90}\text{Sr}$  determination would be false positive.

It is necessary to investigate the quantitative separation of potassium for the ion exchange chromatography on the one hand and the amount of potassium in the precipitate of strontium sulphate on the other hand. The determination of potassium is done by using an ICP-OES system (Inductively coupled plasma optical emission spectrometry).

Potassium is incorporated generally by creatures. The incorporation pathway is soil-plants-food due to its excellent solubility in water.

### 1.2 Optical emission spectrometry

The ICP-OES is a very multifunctional and extreme sensitive technique. It is possible to determine many different elements in many kinds of matrices in the presence of other elements. The sample must be dissolved to be suited for the ICP-OES system available. The sample solution is sucked by a pump system and transported into an argon plasma. This plasma has temperatures from about 5000 to 10000 K. The high temperature causes a breakdown of all chemical compounds into atoms and ions and additionally excites them. The resulting emission of light is spectrally fractionized and a readout of element specific wavelengths gives a qualitative information, if a certain element is included in the sample or not. Quantitative information about an element can be obtained by measuring the intensity of a corresponding wavelength. For this procedure a suited calibration is necessary.

### 1.3 Methods and results

#### 1.3.1 Potassium in the precipitation of strontium sulphate

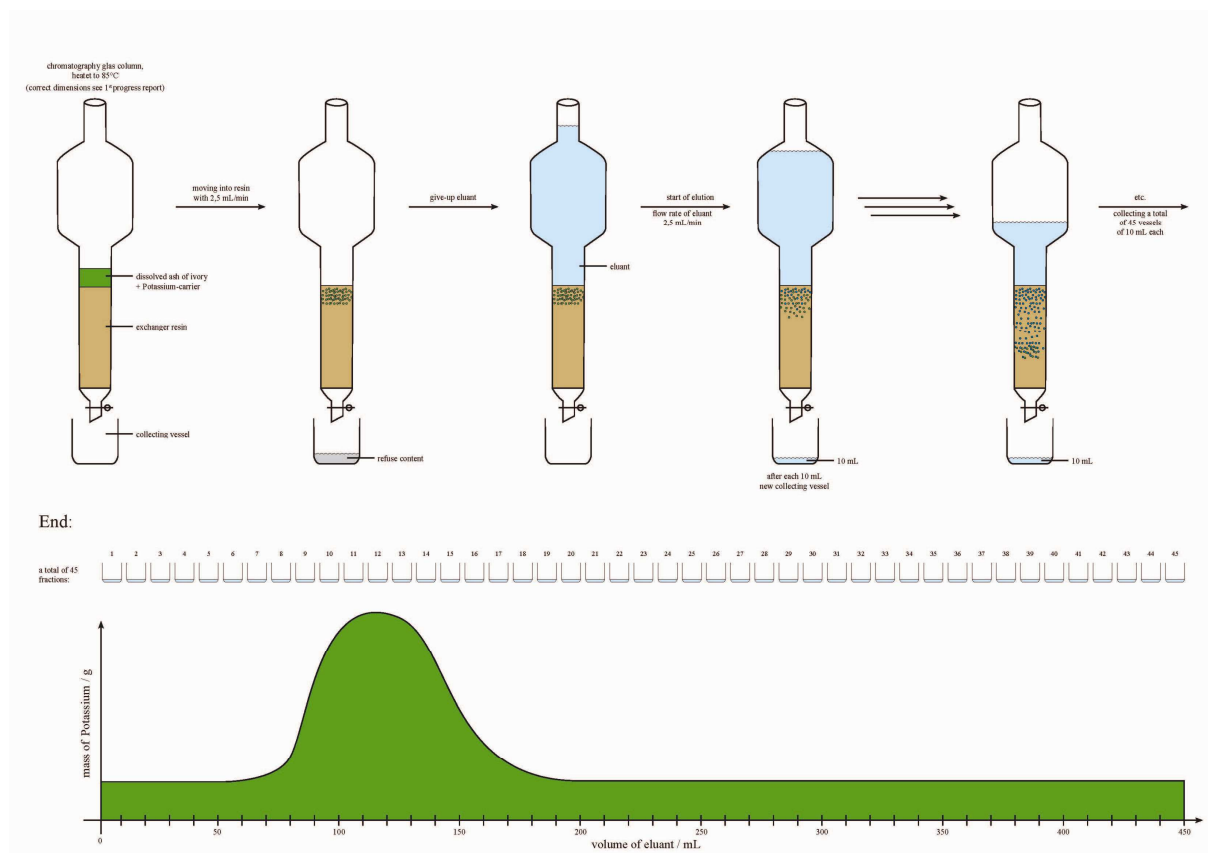
The result of the strontium analysis is a precipitate of strontium sulphate (dry chemical) (see 1<sup>st</sup> progress report). The precipitate must be solubilised to determine the content of potassium. The solubilisation is made with aqua regia (nitrohydrochlorid acid). For this purpose approximately 20 mg of strontium sulphate are weighed in a teflon-vessel and are filled up with 6 mL hydrochloric acid (37%) and 2 mL nitric acid (65%). The chemical digestion is done by boiling and stirring until the yellow orange staining fades. The solution is filled up to 50 mL with water after cooling. That way a solution is achieved, in which both strontium sulphate and maybe present potassium is completely dissolved. The content of potassium in this solution can then be measured using the ICP-OES system.

Up to now the content of potassium was determined in six samples, according to the described procedure. The result are the same for all samples, the content of potassium is below the limit of detection (LOD). The contribution of  $^{40}\text{K}$  to the count rate of  $^{90}\text{Sr}$  is therefore at most 0.005 cpm. But the average background count rate is  $(0.5 \pm 0.1)$  cpm, so the contribution of  $^{40}\text{K}$  is negligible. This shows that the amount of potassium in the  $^{90}\text{Sr}$ -measuring compounds is so small that the count rate is not affected by  $^{40}\text{K}$ .

### 1.3.2 Range of elution of potassium

The range of elution of potassium is identified in a similar procedure according to identifying the elution range of thorium (see 1<sup>st</sup> progress report). Potassium chloride acts as a stable carrier and each elution is sectioned in 45 fractions. Each fraction has a volume of 10 mL. Potassium chloride as a stable carrier is necessary for increasing the natural level of potassium, which is very low, to facilitate the ICP-OES measurements. The more potassium is present, so much the better it is able to be detected by the ICP-OES system. Eight elutions were made. Six of them contain potassium chloride as a carrier, the two others act as background and contain no potassium chloride. The resulting fractions were prepared for measurements in the ICP-OES system. Up to now three of six elutions are already measured but the results will be presented in the following progress report when all measurements are finished.

Following graphic clarifies this proceeding. A diagram results at the end of every elution with what the range of elution of potassium can be read off. The following graphic is only an example and does not show the correct data. Therefore the scaling of the ordinate has not been carried out. This example would determine the range of elution of potassium from approximately 70 mL to 190 mL (see peak). This peak is relative high because of the addition of stable potassium. Being composed of glass, the chromatography column loses contained potassium at higher temperature. Therefore every of the 45 fractions should contain potassium, even if we do not add stable potassium carrier (background). That is the reason why following graph does not start at the origin. The graphic run for this background is similar to the following one, but the peak between 70 mL and 190 mL strongly loses height.



## 2. Validation of the coupled analysis method

### 2.1 Introduction

The analysis of all nuclides shall be tested using certified standard materials. This enables an estimation of the accuracy of the method. Accuracy is defined as systematic difference of the resulting average value and the denoted, certified values. The used certified standards contain a known activity of  $^{14}\text{C}$ ,  $^{90}\text{Sr}$ ,  $^{230}\text{Th}$  and  $^{232}\text{Th}$ .

### 2.2 $^{14}\text{C}$

The validation of the  $^{14}\text{C}$  analysis is done using a  $^{14}\text{C}$  reference material provided by the International atomic energy agency (IAEA). This reference material is oxalic acid (IAEA C-7) and its  $^{14}\text{C}$  activity is given to be  $(49.53 \pm 0,12)$  pMC (percent modern carbon) pMC (M. Le Clercq et al., 1998. New  $^{14}\text{C}$  reference materials, Radiocarbon, 40(1), 295-297). The analysis is done according to the optimized setup which is described in detail in the 1<sup>st</sup> progress report. Up to now two analysis were carried out. The results are shown in table 1.

Table 1: Results of the analysis of the oxalic acid reference material (IAEA C-7). Uncertainties are calculated according to a confidence level of 95 %.

Number of analysis	Number of measurements	pMC
1	1	48,5 ± 2,9
2	7	51,1 ± 3,0

Both resulting values are in good agreement to the reference value according to the measuring inaccuracy. Some more analysis are planed to verify this result.

### 2.3 $^{90}\text{Sr}$ and Th

Ivory ash is relatively similar to bone ash. A reference material is provided by the National Institute of Standards and Technology (NIST) which consists of contaminated human bone and cow bone ash in a ratio of 1:22. The activities of  $^{90}\text{Sr}$ ,  $^{230}\text{Th}$  and  $^{232}\text{Th}$  within this ash are certified amongst others. It is planned to do four coupled analysis of this ash according to the procedure described in the first progress report. Up to now one analysis is finished already. The results of all analysis will be presented in the next progress report.

## 3. Prearrangements for preparation of a distribution curve of a whole tusk

The distribution of the target nuclides longitudinal within a tusk is determined using a whole tusk (Identification number: TZ-05 MIE 22912 alternatively BfN7, fetched from Montabaur). The tusk is sawed in suited pieces using a band saw. First the whole tusk is divided longitudinal into two pieces, left and right part (Figure 3.1).



Figure 3.1: First cut

Afterwards, the right part is sawed radially in pieces of about 4 cm (Figure 3.2).



Figure 3.2: Further cutting

45 pieces of the right part of the tusk were obtained according to the described procedure (Identification numbers: BfN7\_R1, BfN7\_R2, etc.). The left part of the tusk is stored as reserve at the moment.

#### 4. Acquisition of samples

##### 4.1 BfN23 up to BfN32

These samples were provided by the BfN from different zoos (Basel, Wuppertal and Hagenbeck). The samples are the cone end of elephant's tusks. How valuable these samples are will be turned out after the preparation of a distribution curve of a whole tusk.

##### 4.2 BfN38 up to BfN46

Nine independent dated samples were provided by Stefan Ziegler. All samples were taken on the base of the tusks.

Tab. 4.1: Date of death and masses of the independent dated samples

<b>Internal identification</b>	<b>Date of death</b>	<b>Mass in g</b>
BfN38	2010	11,73
BfN39	2007	10,12
BfN40	2007	13,24
BfN41	1998	18,74
BfN42	1999	12,90
BfN43	1990 od. 1996	13,00
BfN44	1997	11,61
BfN45	1994	9,92
BfN46	2011	12,94

##### 4.3 Enquiries

Further enquiries were done to the Museum of Ivory in Erbach, to the Stuttgart State Museum of Natural History, to the Senckenberg Museum in Dresden, to the Museum für Naturkunde of the Humboldt-University of Berlin and to Dr. Heidecke, University of Halle. Except the universities of Berlin and Halle, the institutes have refused or do not have available useful samples. Dr. Mayer of Berlin will check the inventory contemporary and Dr. Heidecke has not replied yet.

#### 5. Outlook

All aims according to the service description within the actual time period could be completely accomplished. The acquisition of about five further independent dated samples between the nineteen-sixties and nineteen-eighties would be desirable. To this we are looking forward to the reply of the Humboldt-University. Further work in 2011 can be done according to the service description.

- Testing the separation of  $^{40}\text{K}$  from the  $^{90}\text{Sr}$ -measuring sample up to September 30<sup>th</sup> 2011
- Validation of the coupled analysis method of  $^{14}\text{C}$ ,  $^{90}\text{Sr}$  and  $^{228/232}\text{Th}$ , up to October 31<sup>th</sup> 2011
- Screening of ivory for other nuclides (e.g. lead-210, nickel-63, plutonium-239/240, plutonium-238, plutonium-241) which could be useful for dating purpose, too, up to December 31<sup>th</sup> 2011

If applicable, the determination of the distribution curve will be started already in 2011 (this step is preferred to be done before the step “Validation of the method using samples of known age” caused by scientific reasons).