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Fingerprinting of ivory and horn through the application of nuclear analytical techniques

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The feasibility of fingerprinting elephant ivory and rhino horn to establish the origin and accordingly promote the sale of legally stockpiled reserves from South Africa into the (closed) world markets have been investigated in the past, and preliminary studies with non-nuclear techniques look promising. The Research Reactor programme within the framework of AFRA is currently becoming bent on applications of nuclear analytical techniques for socio-economic development. It is as part of this AFRA programme, that instrumental neutron activation analysis can possibly be used as a powerful and reliable fingerprinting technique for the determination of the origin of ivory.

Introduction

Ivory has been a popular commodity for ages in the manufacturing of jewellery and other works of art. African and Asian elephant ivory is difficult to distinguish from one another, yet professional artists claim that the former is more suitable for carving. Poaching has furthermore seriously disrupted the breeding patterns in some elephant herds, as the big tuskers, normally the older males, are picked off selectively. Civil wars in Africa also had an incalculable toll on free roaming elephant. All of these evidently contributed to the almost total demise of the African elephant. Prior to 1989, the annual trade in raw ivory was estimated to be between 600 and 800 tonnes, representing some 50,000 elephants. The total elephant population on the African continent decreased by over 50% within a ten-year period up to 1989.

Then, in October 1989, at its biennial meeting in Lausanne, Switzerland, the Convention on International Trade in Endangered Species (CITES) called for a total ban on the trade in elephant products. At the 1997 CITES meeting in Harare, Zimbabwe, the Southern African countries succeeded in passing a resolution which allowed Namibia, Botswana and Zimbabwe to sell limited stock to Japan.

The elephant population in Southern Africa is undisputedly growing, despite poaching not being completely eradicated. Their recovery is the result of the establishment of well-managed game sanctuaries and a steady elephant population growth each year. The National Parks Board of South Africa has given intention of applying for permission through CITES to sell off its stockpile of ivory at the Kruger National Park, using the money for nature conservation.

Whether limited trading is allowed or banned outright, both approaches would require a reliable method to determine the origin of ivory. One of the projects within the IAEA-AFRA regional African framework is focussed on the utilization of Research Reactors for socio-economic development. Since this project is currently focused on the application of nuclear analytical techniques, neutron activation analysis, as a powerful fingerprinting technique, will be explored for its applicability to classify ivory and other horn species. Furthermore, participation by other African countries is foreseen, so that the African people can take charge and contribute to saving an animal that symbolizes Africa in so many aspects.

Objective of this study

Elephant ivory with a confirmed origin is difficult to come by, and a preliminary study was therefore launched on available materials, which included ivory samples from a variety of African wildlife. This study was to focus on the following aspects: (1) sample preparation and possible contamination, (2) inherent inhomogeneity of the sample matrix, (3) fingerprinting of the various tooth and ivory matrices and (4) possible presence of naturally occurring radionuclides in ivory.

Experimental

Sampling

The following sample matrices are being investigated for this study:

Warthog tusks: Unlike elephant ivory, these have an enamel coating over the underlying dentine. Growth layers are visible as concentric rings and a small pulp cavity exists in the middle of the tusk, which forms part of the root and also accommodates the nerve endings.

Hippopotamus ivory: The canine normally consists of two layers of dentine: an outer, primary layer and an inner, secondary layer. For the samples analysed, these layers could not be distinguished with the naked eye. Pulp cavities are fairly large. A thick enamel coating

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covers the underlying dentine. This could be removed relatively easily and also analysed separately from the dentine.

Elephant ivory: Samples from different specimens (origin unknown) were received for analysis. Elephant tusks do not have an enamel coating. They do have a cementum layer, however, a bone-like tissue in which the whole tooth is embedded, also called the "bark" or "rind". Samples were taken from a cross section of a tusk, not distinguishing between the concentric oval growth lines (lines of Owen) typically found in a cross section of a tusk.

A section from the base of an elephant tooth, where the pulp cavity is large and the dentine layer thin, was also analysed.

Sample preparation

Sub-samples were prepared by cutting thin 1 to 2 mm layers of ivory/tooth from the bulk samples by means of a diamond coated electric saw. All sub-samples were merely wiped with an ethanol-soaked tissue paper. Sub-samples were handled with surgical gloves and plastic tweezers.

Instrumental neutron activation analysis (INAA)

Analysis: Sub-samples of 300 to 700 mg were weighed out in special high-purity polyethylene irradiation capsules. These were sealed ultrasonically, individually issued with an iron flux monitor, and transferred to a polyethylene rabbit for irradiation in one of the pneumatic rabbit systems (PRS) of the SAFARI-I Research Reactor at Pelindaba. Samples were irradiated for 30 minutes each at a neutron flux of about $2 \cdot 10^{13}$ n·cm^{-2} s^{-1}.

In general, samples are left for 7–9 days after irradiation before transfer to clean capsules and before counting of samples commence. The ivory samples had to be left for at least 16 days before counting could start, due to the high specific activity of the samples. This was caused by the relatively high phosphorous content of the dentine.

Samples were eventually counted on a HPGe well-type detector with an automatic sample changer for one hour per sample. No element standards were included for this initial study.

Results

Results are reported in Table 1 for a few essential and trace elements for the different specimen analysed. Results were normalized to that of an elephant ivory sample.

The following observations can be made:

(1) Calcium is a major component of ivory. It appears as if the calcium concentration were the lowest in elephant ivory and almost twice as abundant in warthog and hippopotamus ivory. The elephant tooth base sample also has a higher calcium content, probably because the cementum to dentine ratio is much higher. Cementum resembles bone and is expected to have a high calcium content.

(2) Cobalt varies considerably from sample to sample. The estimated cobalt concentration, however, is less than one part per million for elephant ivory, and inhomogeneity of the sample material, as well as contamination of the samples during sample preparation could contribute to this observed variation.

(3) Iron and zinc also appears to be more concentrated for warthog and hippopotamus, and, in the case of iron, significantly concentrated for the tooth base sample. Contamination during sample preparation could contribute to this variation.

(4) The two elephant ivory samples (example 1 and 2) have more or less the same concentration of elements, except for cobalt and iron, which appears to vary by a factor 3 to 40. As stated before, contamination during sample preparation could contribute to this variation.

(5) It is important to realise that the above observations were made on the grounds of a single, or at the most, a triplicate analysis. The possible in-homogeneity of the ivory and tusk matrices should still be investigated.

Since the enamel could be easily separated from the bulk dentine in the case of the hippopotamus ivory, it was analysed separately. Results are reported in Table 2 and are normalized to that of the hippopotamus dentine sample. It appears as if most of the observed elements were more concentrated for the enamel sample, with the only exception being zinc. This study shows that sampling of ivory should be performed with great care and that the term "representative sampling" be defined clearly, if possible, for ivory and tooth sample materials.

Epithermal irradiation

Phosphorus is one of the major constituents of tooth and ivory and interferes with the analysis of minor and trace elements by INAA due to the formation of ^{32}P ($T_{1/2} = 14.5$ d). ^{32}P decays to ^{32}S and in the process high-energy (1.7 MeV) β-particles are emitted which causes bremsstrahlung on interaction with surrounding matter. Furthermore, special shielding is required to protect analysts from the high-energy β-radiation and protect counting equipment from the bremsstrahlung interference.

Table 1. Element constituents for various ivory matrices

Element	Warthog	Hippopotamus	Elephant example 1	Elephant example 2*	Base of elephant tusk
Ca	1.95 ± 0.49	1.84 ± 0.48	1.10 ± 0.27	1.00 ± 0.26 (–20%)	1.51 ± 0.37
Co	1.16 ± 0.22	0.93 ± 0.15	3.45 ± 0.41	1.00 ± 0.15 (–0.1 Φg/g)	19.5 ± 2.2
Fe	2.64 ± 0.89	2.54 ± 0.87	39.3 ± 10.5	1.00 ± 0.37 (–50 Φg/g)	455 ± 120
Hg	<2.2	<1.6	<1.0	1.00 ± 0.33 (–50 Φg/g)	<1.3
Sc	>0.65	>0.67	>4.0	1.00 (–0.2 Φg/g)	>1.7
Sr	1.38 ± 0.15	1.33 ± 0.10	0.62 ± 0.07	1.00 ± 0.08 (–500 Φg/g)	0.67 ± 0.06
Zn	2.57 ± 0.11	1.58 ± 0.07	0.75 ± 0.04	1.00 ± 0.04 (–100 Φg/g)	2.03 ± 0.08

* Estimated concentration values for elephant ivory are given in brackets for each element.

Table 2. Variation in element composition for hippopotamus dentine and enamel

Element	Hippopotamus ivory dentine	Hippopotamus ivory enamel
Ca	1.00 ± 0.29	1.84 ± 0.48
Co	1.00 ± 0.30	0.93 ± 0.15
Fe	1.00 ± 0.32	2.54 ± 0.87
Sc	1.00 ± 0.17	1.77 ± 0.28
Sr	1.00 ± 0.06	1.69 ± 0.14
Zn	1.00 ± 0.05	<0.14

Table 3. R_{Cd} values and advantage factors for a suite of radionuclides

Element	Radionuclide	R_{Cd} value	Pseudo "R_{Cd}" value	Advantage factor
Ba	^{131}Ba (215 keV)	4.59	3.76	0.82
	^{131}Ba (496 keV)	4.60	3.54	0.77
Ca	^{47}Ca (1297 keV)	19.14	1.70	0.09
	^{47}Sc (159 keV)	19.14	3.79	0.20
Fe	^{59}Fe (1099 keV)	15.62	2.28	0.15
	^{59}Fe (1292 keV)	16.31	1.67	0.10
	^{54}Mn (834 keV)	2.27	2.97	1.31
Sr	^{85}Sr (513 keV)	5.18	3.44	0.66
Th	^{233}Pa (300 keV)	6.26	3.67	0.59
	^{233}Pa (311 keV)	6.31	3.68	0.58

Due to the above analytical restrictions, the possibility of epithermal irradiation was also investigated. The laboratory operates a pneumatic irradiation system that offers either unshielded irradiation, where a sample is exposed to the full neutron spectrum, or a cadmium-shielded irradiation position, whereby only the epithermal neutrons pass through. If the interfering radionuclide has a higher cross section for thermal neutrons than the radionuclides of interest, the activation of this interfering radionuclide would be suppressed relative to the radionuclides of interest.

The investigation was performed by irradiation of a number of element standards, including phosphorus, in both the unshielded and cadmium-shielded positions. R_{Cd} values are then calculated for each radionuclide of interest. A R_{Cd} value is defined as:

$$R_{Cd} = \frac{\text{Specific activity (Bq/g) in the unshielded position}}{\text{Specific activity (Bq/g) in the CD - shielded position}}$$

Pseudo R_{Cd} values were also determined for each radionuclide of interest in relation to phosphorous by considering the continuum caused by bremsstrahlung in the energy region of the radionuclide of interest. The pseudo R_{Cd} value is defined as:

$$\text{“}R_{Cd}\text{”} = \frac{\text{MDA - value (Bq/g) in a P matrix in the unshielded position}}{\text{MDA - value (Bq/g) in a P matrix in the CD - shielded position}}$$

where MDA is the minimum detectable activity.

The minimum detectable concentration (MDC) of a radionuclide of interest in a phosphorous matrix under irradiation in the unshielded position can now be calculated and compared to that for irradiation in the shielded position. This advantage factor is defined as:

$$\text{Advantage factor} = \frac{\text{MDC - value (g/g}_p\text{) in the unshielded position}}{\text{MDC - value (g/g}_p\text{) in the Cd - shielded position}} = \frac{\text{Pseudo "}R_{Cd}\text{" - value}}{R_{Cd}\text{ - value}}$$

where MDC is the minimum detectable concentration.

For some radionuclides of interest, the R_{Cd} value, pseudo "R_{Cd}" value and advantage factor are reported in Table 3. For the suite of radionuclides investigated, it can be seen from Table 3 that the advantage factor is less than one, which implies that with epithermal irradiation the radionuclide of interest is suppressed more than with thermal irradiation for a phosphorous matrix. The only exception is ^{54}Mn, which forms by the (n,p) reaction from ^{54}Fe. This is expected, since (n,p) and (n,γ) reactions normally benefit from epithermal irradiation. From this investigation it can be concluded that there is probably no real advantage in epithermal irradiation in order to minimize interference from phosphorous.

NORM analysis

The possible presence of Naturally Occurring Radioactive Materials (NORM's) in ivory and tusk samples were also investigated, since the abundance of these radionuclides vary significantly in the Southern African region.

Analysis

One sub-sample of 15 g was prepared from the elephant ivory sample labeled Elephant example 2. This sub-sample was prepared by cutting thin cross sectional layers of ivory from a tusk and adjusting this to a specific calibrated sample geometry. The sample was then counted on a low-background HPGe gamma detector (20% relative efficiency) for a counting period of 24 hours. The measured results are reported in Table 4.

Table 4. Naturally Occurring Radioactive Materials (NORM's) in elephant ivory

Radionuclide	Specific activity, Bq/kg
^{226}Ra	19.6 ± 5.6
^{228}Ra	<35
^{228}Th	14.9 ± 4.6
^{40}K	143 ± 77

It would appear that some of the NORM's are present in ivory. Since the concentration of these radionuclides in mammals are linked to diet, it is important to also study drinking water and food of elephants for the typical NORM's.

Future studies planned

The preliminary study discussed in this paper, identified a number of important issues that should be investigated further:

Tooth and ivory matrices are inhomogeneous and the extent thereof should be investigated thoroughly. Rhino horn was not available for this study and should be included for future investigations. Unlike ivory, rhino horn is made up of hair and is quite different to dentine.

The individual growth layers of calcified tissue (Lines of Owen) of an elephant tusk should be studied for differences in elemental composition.

Since the diet of an animal, especially its drinking water intake, has an influence on the chemical composition of its dentures, samples of drinking water and typical food should also be investigated.

The natural radioactivity content of ivory should be investigated further. This should include the analysis of ^{238}U, ^{235}U, ^{232}Th and their respective progenies.

The possible presence of the anthropogenic radionuclides ^{89}Sr/^{90}Sr should be investigated for ivory.

Short- and intermediate-lived nuclides are to be investigated as well to obtain an overall picture of the potential of INAA for fingerprinting ivory and horn specimen. Accordingly, the advantage factors for epithermal activation should be studied for more elements of interest.

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