NON—DESTRUCTIVE MEASUREMENTS OF LEAD AND BARIUM IN ARCHAEOLOGICAL BONE SAMPLES USING XRF

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ABSTRACT

The lead and barium contents in sixteen archaeological bone samples from 10 persons buried in Dalsby, Sweden, were determined by means of X- ray fluorescence analysis using two ^{57}Co sources for excitation and a planar Ge detector for registration of the X- rays. The lead concentrations were found to be less than 168μ g/g, and the barium concentrations were in the range of 15- 97μ g/g.

Keywords: X- ray fluorescence analysis Lead Barium Archaeological bone

I. INTRODUCTION

Elemental analysis of human bones from archaeological sites helps in the assessment of dietary and disease history of the studied population[1,2].

For rare archaeological sample it is important to use a non- destructive analytical technique. With XRF it is possible to measure the concentrations of, for example, lead and barium down to several μ g/g.

The purpose of this work was to study the lead concentrations in bones from persons buried at the grave yard of Dalsby, a parish in a mining district of central Sweden in the 16th and 17th centuries. We also wanted to study the origin of considerable barium levels found in these bones and in other archaeological human bones.

II. MATERIALS AND METHODS

The bone samples were provided by the Historical Museum in Stockholm. Sixteen bone samples from 10 individuals were analysed. The approximate ages of the individuals were osteologically determined (Table 1).

The measurement of barium and lead was carried out using two ^{57}Co sources in opposite positions. The total activity is about 0.6 GBq. The characteristic X- rays were detected by an HP germanium detector (16mm x 5mm) placed at 90° to the incident gamma rays. The experimental set up is shown in Fig.1. The signals were amplified and analysed by an MCA. From the XRF spectra net counts of the Ba and Pb K_x peaks and the coherent peak were determined, as was the number of counts in

the central region of the incoherently scattered photons.

Table 1

Measured Ba, Pb and mineral concentrations in archaeological bones from Dalsby, Sweden

ID	"Age"	Sample No.	Type of bone*	Ba concentration (μ g/g)	Pb concentration (μ g/g)	Mineral concentration(%)
		1	rib (3)	91±12 (108±14)	13±17 (16±20)	86±5 (44±9)
A	Child	2	vertebra (2)	46±20 (65±28)	3±27 (5±38)	118±9 (38±19)
		3	vertebra (6)	26±10 (30±11)	0±14 (0±16)	73±4 (39±7)
B	Young	4	ulna (4)	97±11 (111±12)	19±15 (22±17)	94±5 (61±7)
		5	vertebra (10)	68±5 (71±5)	14±8 (14±8)	71±20 (60±3)
C	Young	6	rib (5)	90±10 (102±11)	14±14 (16±16)	85±4 (53±7)
D	Child	7	clavicle (4)	15±11 (17±13)	24±15 (28±18)	93±5 (57±8)
E	Adult	8	phalanx (8)	28±6 (30±7)	127±10 (136±11)	73±3 (56±4)
		9	phalanx (7)	16±5 (16±5)	168±8 (177±9)	83±2 (72±3)
F	Child	10	costa (5)	21±8 (23±9)	17±12 (19±14)	77±4 (51±6)
G	Adult	11	phalanx (8)	37±5 (39±6)	29±8 (30±9)	77±2 (65±3)
		12	phalanx (8)	60±5 (63±6)	22±9 (23±9)	70±2 (57±3)
H	Adult	13	phalanx (7)	60±6 (65±7)	20±10 (21±11)	68±3 (50±4)
I	Adult	14	phalanx (7)	14±5 (15±5)	12±9 (13±9)	69±2 (56±3)
		15	phalanx (6)	50±8 (56±9)	5±12 (6±13)	84±4 (60±5)
J	Adult	16	phalanx (8)	22±4 (23±5)	49±8 (51±8)	65±2 (55±2)

All stated concentrations are by archaeological, dry weight and the stated errors are 1 SD due to counting statistics. In parentheses are given the concentration values after correction for the coherently and incoherently scattered photon count rates with no sample.

* The values in parentheses are the approximate mean diameters (mm) of the bone sample at the point of measurement.

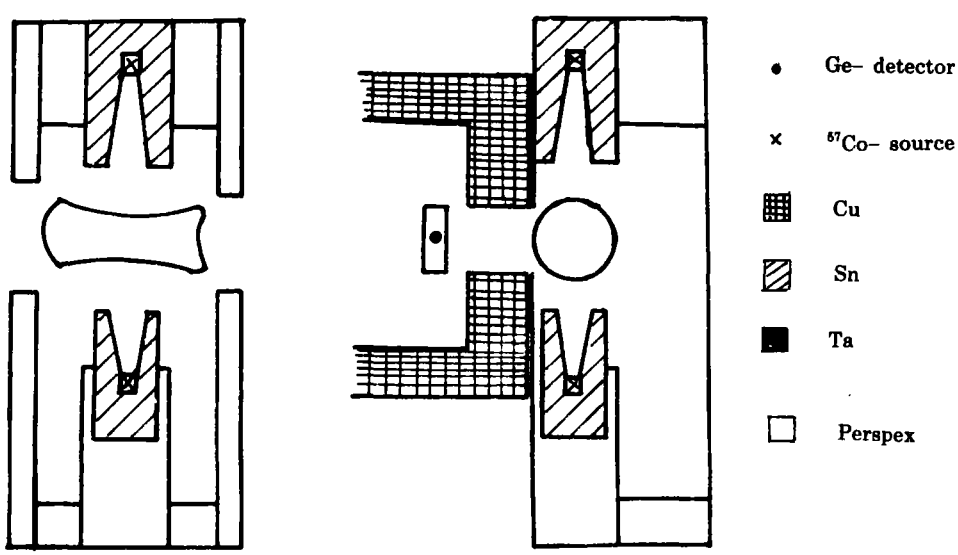

Fig.1 The arrangement for the determination of barium and lead in bone by X—ray fluorescence analysis

The Ba and Pb concentrations were estimated by using the ratio of their K_α

X- rays and the incoherently scattered radiation. And at the same time the bone mineral concentration was estimated using the ratio between the coherently and incoherently scattered primary photons. The approach was described in detail by Ahlgren et al[3,4].

For calibration purpose water solutions with known concentrations of barium and lead were used. Distilled water was used to represent a zero concentration of barium, lead and bone mineral, while bone ash was used to represent a bone mineral concentration of 100%. The calibration measurements were done with 5 ml cylindrical plastic containers (22mm in diameter and 1mm in wall thickness). This well covers the effective measuring volume, as the collimators of the sources and detector intersect just a volume of approximately 2 cm^3.

Because the quotient between the count rate of the characteristic K_α X- rays of lead and the incoherently scattered photons is independent of the density and of the atomic composition of the surrounding matrix[4], these calibration results are valid for bone samples of various densities.

All the bone samples were analysed at the midpart. The measuring time was 10800s (3 h) which gave a minimum detectable limit (MDL) of 4 and 7 μ g/g dry weight for Ba and Pb respectively.

III. RESULTS AND DISCUSSION

The Ba, Pb and mineral concentrations are given in Table 1 and Fig.2.

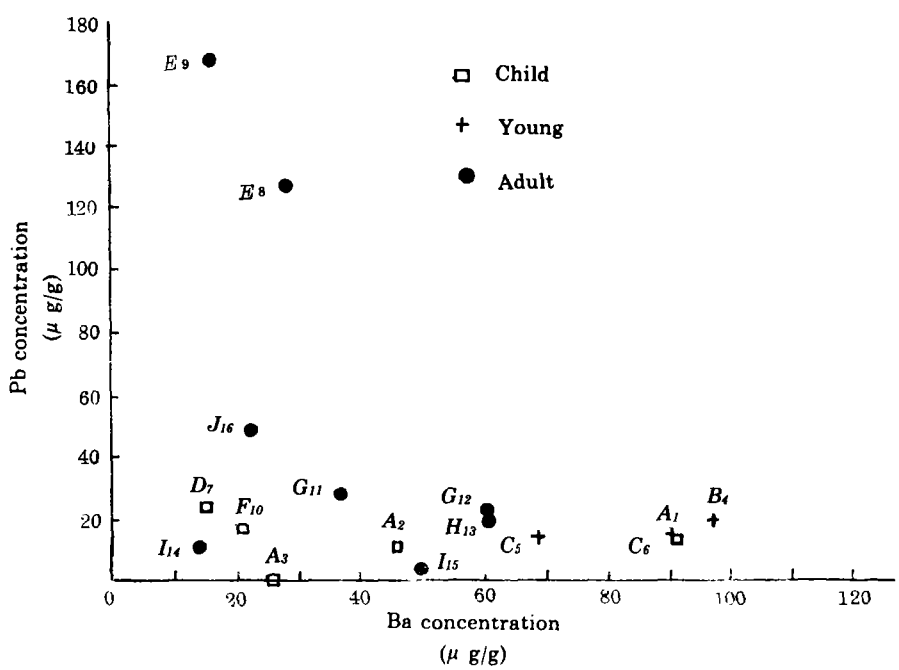

Fig.2 The lead and barium concentrations of 16 archaeological bones

As seen in Table 1 and Figure 2, the lead concentrations in different bones from the same individual vary within the range of the statistical fluctuations of the measurements. On the contrary the barium concentrations in different bones from the same individual show remarkable variations, especially for individuals *A* and *I*.

The children and young people had low Pb concentrations (<30 μ g/g dry weight, or <15 μ g/g wet weight)[4]. The Pb concentrations in the most contaminated individuals were of the same order (120– 170μ g/g dry weight, 60– 90μ g/g wet weight) as the maximum values measured in smelter workers of present days[5].

By comparing the lead and barium concentrations with bone mineral concentrations of the same individual, it is seen that lead concentrations are correlated, to some extent, to the bone mineral concentrations. The barium, however, shows less correlation to the bone mineral concentrations. This may indicate to some extent that barium originated from external contamination in the soil.

One of the high Pb concentration samples (No. 8) and one of the low Pb concentration samples (No. 14) were analysed at different midparts of the sample, with the sample rotated 90° between the measurements. The results are shown in Table 2.

Table 2

The measured Ba, Pb and mineral concentrations at different orientations*

Position	Ba Concentration* * (μ g/g)	Pb concentration* * (μ g/g)	Mineral concentration* * (%)
1	25±6	131±9	72±2
	(10±5)	(30±9)	(72±2)
2	12±6	108±9	69±2
	(18±5)	(0±8)	(77±2)
3	27±5	142±8	74±2
	(15±5)	(20±8)	(70±2)
4	20±5	132±9	74±2
	(17±5)	(3±8)	(69±2)

* The stated errors are 1 SD due to counting statistics.

* * Values above parentheses indicate the measured results of sample No.8, a phalanx, approximately 8 mm in diameter at the point of measurement. Values in parentheses indicate the measured results of sample No.14, a phalanx, approximately 7 mm in diameter at the point of measurement.

No significant difference could be found in the Ba, Pb and mineral concentrations of different orientations (the values are in accordance with each other within the range of ± 2 SD), hence a homogeneous irradiation (analysis) has been achieved. That also implies that the effect due to the inhomogeneous distribution of Ba and Pb in bone samples is insignificant.

The lead concentrations in some samples were measured two years earlier with the same experimental set up, so it was possible to estimate the reproducibility of the technique.

The results of duplicate Pb measurements on 11 bone samples are shown in Fig.3.

The reproducibility is fairly good, with the standard diviation of the differences being about 4 μ g/g dry weight.

It should be noted that air measurements (with no samples) of the XRF set up showed that there is always a contribution of coherently and incoherently scattered photons. The "background" contributions are scattered photons from different parts of the experimental set up, i.e. the source collimators, perspex holder and detector collimator. Correction can be made by subtracting these "background" count rates from the sample measurements. The results of such a correction are shown in Table 1 as values within parentheses.

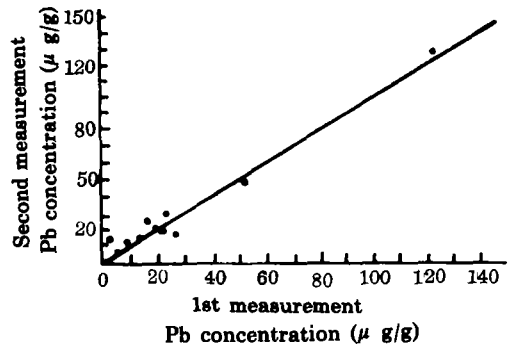

Fig.3 The reproducibility of lead measurement on 11 bone samples

The calculation method in this work conformed to the approach adopted in Ref.[4], in which the background correction was omitted. The correction decreased significantly the bone mineral concentration. For small diameter bone samples, the corrected result may be up to three times lower. Therefore further work is needed to verify the method on background corrections.

REFERENCES

[1] J.H.Kyle, *J. Arch. Sci.*, **13** (1986), 403.

[2] L.E.Wittmers et al., *Arch. Environ. Health*, **43** (1988), 6:381.

[3] L.Ahlgren et al., *Phys. Med. Biol.*, **24** (1979), 1:136.

[4] L.Ahlgren et al., *Adv. X Ray Anal.*, **24** (1981), 377.

[5] J.O.Christoffersson et al., *Am. J. Ind. Med.*, **6** (1984), 447.