

## Tin in Human Bones

Jaroslav Jambor<sup>\*</sup>, Václav Smrčka<sup>\*\*</sup>

### Abstract

TIN IN HUMAN BONES. The tin content in the bones of 149 skeletons from the 1st - 5th centuries A.D., and of 11 individuals of the recent population was determined. The bone samples were carbonized and analyzed through emission spectroscopy with a.c. excitation. The tin content in bones of recent populations not exposed to extra tin supply is about one order of magnitude higher than is the case with the bones of some populations that lived at the beginning of our era. The distribution of tin in long bones, dependent on age, as well as the sources and role of tin in environmental contamination are discussed.

Jaroslav Jambor, Václav Smrčka, 1993; *Polish Anthropological Review*, vol. 56, 1-2, Adam Mickiewicz University Press, Poznań 1993, pp. 151-156, fig. 1, tables 2. ISBN 83-232-0524-8, ISSN 0033-2003.

Tin is not considered to be an important element from the viewpoint of alimentation. The guide values of permitted tin contents in foodstuffs are very high and sometimes they are not determined at all. The considerable discrepancies in the data concerning tin content in human tissue resulted in the requirement to determine the real tin concentrations in the bones of populations in the past, and also in the present generation and to check the ways of depositing Sn in the long bones of human beings.

### Material

A total of 278 samples of femurs, tibiae and pyramids of the petrosal bones from 113 skeletons of Central European burials

and of 36 African skeletons (Egyptian Nubia) from the period ranging from the 1st to the 5th century A.D. were taken.

From 5 cadavers of the contemporary generation in the Brno Region (South Moravia), aged 21, 37, 55 and 78 years who died in accidents we took 11 samples of femurs and tibiae of the right and of the left legs. From the heads we separated samples of compact and cortical bones.

A further group of the contemporary population was formed by 6 individuals with peroperationally removed bone samples (traumatic amputees or unused remnants of bone implants).

The bone samples were taken with the help of surgical instruments, Liston's and Luer's bone nippers, and from cadavers with the help of electric saw and chisel.

The skeletal material from the 1st - 2nd centuries is deposited in the National Museum in Prague (burials in Abrahám, Sládkovičovo and Gerulata II). The skeletal material from the 3rd-5th centuries

\* Department of Analytical Chemistry, Masaryk University  
Kotlařská 2., 611 37 Brno, Czech Republic

\*\* Plastic Surgery Department, Masaryk University  
Berkova 34., 612 00 Brno, Czech Republic

used for the analyses is deposited in the Slovak National Museum (burials Gerulata I and III) and in Landesmuseum für Vorgeschichte in Halle, Germany (burials in Niemberg and in Erfurt). The African skeletal material comes from the 3rd-5th centuries and is kept in the Náprstek Museum in Prague (the Wadi Quita burial in Egyptian Nubia).

## Method

The bone samples were analyzed with the method of emission spectroscopy [JAMBOR 1988]. The samples were carbonized at 250-280°C, pulverized and poured on graphite electrodes. We used a Zeiss PGS 2 spectrograph excited with alternating current, then we evaluated the proportion of intensity between Sn 317.5019 nm line and Ca 299.496 line. The detection limit with this procedure is 0.10 µg Sn in 1 g of samples. On assessing the results it is necessary to take into account the burial outfit. It may have locally contaminated the bones with corrosive products even of objects with low tin content in the soil of the burial ground. The differences in the concentration of tin between the right and left limb, cancellous and cortical bones in the heads of femurs and tibiae, and the determination of the distribution of tin in the long bones were evaluated with the help of dispersion analysis, t-test and pair test.

## Results

Tin in 1.-5. century A.D. Central European populations appears in concentrations up to 1 µg g<sup>-1</sup> of the bones. Unique cases of higher concentration are caused by the presence of bronze objects in the

burial and in these cases we observe also increased content of other elements, namely of copper (Abrahám 1st-2nd century). There is remarkable tin content also in bones found in burials containing silver burial gifts (Niemberg, Erfurt 3rd-5th century).

In the skeletons from Egyptian Nubia of the 3rd-5th century the tin content was below perception limit, i.e. below 0.10 µg · g<sup>-1</sup>.

A survey of tin content in the individual burials is indicated in Table 1.

Table 1. Values of tin content in the bones at the individual burial grounds

Burial Ground	Time of burial (century of our era)	Number of the samples	Tin content in µg g <sup>-1</sup>	
			mean $\bar{x}$	max. value
Wadi Qutina	3-5	44	—	0.1
Sládkovičovo	1-2	12	0.16	0.4
Gerulata II	1-2	65	0.19	0.7
Gerulata I	3-4	53	0.21	1.0
Gerulata III	3-4	25	0.22	0.7
Abrahám	1-2	17	0.26	0.9
Halle	3-5	30	0.32	1.4

Values not reaching detection limit are regarded as 0.10 µg · g<sup>-1</sup>.

Compared with populations from the beginning of our era the tin-content level is higher, individually there are oscillations within broad limits, as indicated in Table 2.

The tin content did not depend statistically in any of the age groups on whether the sample was taken from the left or right leg.

No statistically significant differences have been found in the concentrations of Sn between the spongy matter and the compact heads of femurs and tibiae. We found a difference in the concentration in the compact bone of the heads as compared with the compact bone in the central part of the diaphyses of the long bones.

**Table 2.** Tin concentration at the sample places of femurs and tibiae in  $\mu\text{g} \cdot \text{g}^{-1}$  of bones in four cadavers whose age ranged from 21 to 55 years

Sample place (fig. 1)	1	2	3	4	5	6	7	8	9	10	11
$\bar{x}$	16.4	10.8	5.6	2.9	9.3	10.5	7.9	10.1	3.3	8.8	8.5
$\pm s$	9.6	7.1	5.2	1.5	7.1	11.1	5.9	9.1	2.0	6.8	7.4

The concentration of Sn was higher in the heads than in the diaphyses. The difference in concentrations between the proximal and medial part of femur diaphyses equals significance level  $\alpha = 0.05$  and  $\alpha = 0.01$ . The differences in concentration in the distal part of femur as compared with the medial part and in the two epiphyses in the tibiae compared with the medial part are of significance level  $\alpha = 0.05$ .

The samples of this group were formed by phalanges and parts of hip bones. The number of these individuals was very low and the available bone samples were heterogeneous. It is therefore difficult to compare the two sets of results or to draw conclusions of a general character. The importance of the group consists in the fact that it enables retrospective anamnesis of the eating habits and working environments of each individual.

The tin content in the samples of this group oscillated between  $1\text{--}40 \mu\text{g} \cdot \text{g}^{-1}$  of the bones.

Four individuals with low tin concentration (between  $1\text{--}2 \mu\text{g} \cdot \text{g}^{-1}$ ) were not in contact with tin at all and they consumed canned goods in exceptional cases only (the highest frequency was 5 times per annum). One member of the sample group occasionally soldered radiotechnical components with tin-lead solder.

The second part of the group was formed by two individuals showing higher tin content. A nineteen-year old male, farm machinery repair man, spent a whole workday once a week in a brazing workshop, showed a concentration of  $14 \mu\text{g}$

Sn in 1 g of bone. Tin is not used for brazing, but solders contain some tin in the form of impurities, which at temperatures above  $600^\circ\text{C}$  appears in the fumes. This individual also ate canned goods only exceptionally.

The other individual was a forty-two year old male with  $40 \mu\text{g} \cdot \text{g}^{-1}$  of tin in his bones. He drank canned juices at regular intervals – once a week. He had no contact with an environment contaminated by tin.

## Discussion

Tin is distributed in human long bones in the same way as other metal elements. The maximum concentration is at the end parts of the long bones, while in the compacts of the medial part the concentration is the lowest. Many of these elements, such as Zn, Cr, V and others have great importance for the growth. The influence of tin on growth has only been described in rats [SCHWARZ et al. 1970].

We would deduce from the course of dependences (Fig. 1) that there exists a certain dependence between the concentration of tin in the long bones and between age. There is no tin at all in the tissue of still-born children [SCHROEDER et al. 1964], in the group we were following we found the highest concentration in the 3rd and 4th decade of age, and following the 50th year of age there is a sudden drop in tin content. An elderly individual (78 years old), whose data are not

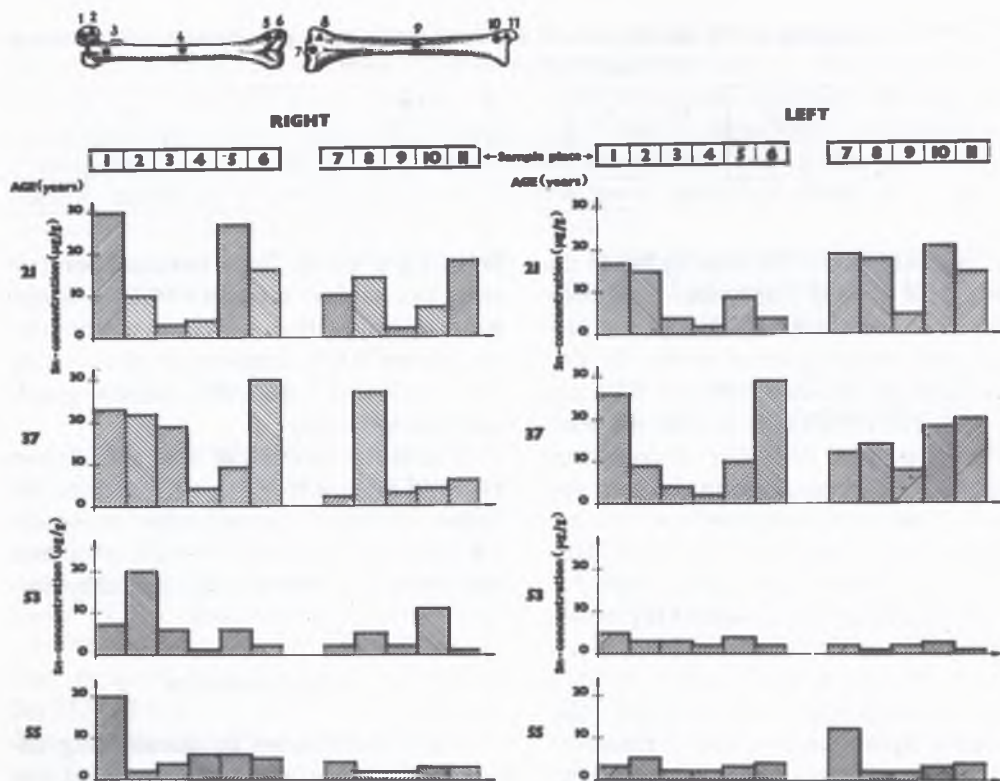


Fig. 1. The distribution of Sn in femurs and tibiae in connection with age, long axis and lateralization. (The diagram shows sampling places - 2, 6, 8, 11 cancellous bone; 1, 3, 4, 5, 7, 9, 10 compact bone)

indicated in the graph, had a tin content of  $1 \mu\text{g} \cdot \text{g}^{-1}$  in his bones. However, from such a small number of samples we cannot draw conclusions; this dependence probably reflects the contact (or lack of contact) of the individuals with a contaminated environment and with certain victuals. Newborn children have minimum contact with tin, but it increases gradually and culminates in middle-aged people, at the time of their highest activity in their thirties and forties. As the individual grows older the chances of higher tin input to the organism decrease. This fact, together with the uninterrupted renovation of all tissues, results in a systematic drop of tin content in the body.

It follows from the comparison of the population from the first centuries of our era with the recent population that tin content in the bones has considerably increased. The broad dispersion of content values in various individuals and the generally oscillating tin level in the environment well document that tin belongs to the group of the so-called civilization contaminants. Up to the last century the main unnatural contaminant was lead [ERICSON et al. 1979]. Since the toxic effects of lead on human organisms had been proved and the capability of lead to concentrate namely in bone tissues is known, the lead content of victuals, of all objects that are in contact with victuals, in the environ-

ment, etc. is being systematically checked. Thus it has been possible to curb the supply of lead to the human organism and it has been possible to cut also the lead content in bones. The latest analyses indicate that lead as a contaminant is being replaced at present – besides other elements – mainly by tin, at levels exceeding the level of other metals.

Tin is regarded as a non-toxic metal, it is a poor absorbent and no form of its accumulation is supposed in the organisms [UNDERWOOD 1977]. Our results document that the above assumption is not fully justified. According to the WHO [Evaluation... 1982] a tin dose of up to  $2 \text{ mg kg}^{-1}$  of live weight can be regarded as harmless. This value reflects only the immediate reaction of the organism on a single (non-recurring) tin dose without taking into account possible concentrations and accumulation of tin in the bones or its long-term impacts on biochemical processes.

In the case of lead, it has been proved that there are considerable differences between the natural and normal content of this element. The same holds also for tin, although to a lesser degree. In lead the proportion between normal and natural content was determined with the value of about 1000 [PATTERSON et al. 1987]. In tin the proportion can be put at about 10. The concentration of tin in skeletons in the Egyptian part of Nubia can be regarded as natural; their values were without exception lower than  $0.10 \mu\text{g} \cdot \text{g}^{-1}$  of bone. The normal level at present is the concentration of about  $1 \mu\text{g} \cdot \text{g}^{-1}$  for individuals not exposed to an increased tin supply from foodstuffs and from the environment. The difference compared with lead is caused by the lower geochemical content of tin in the biosphere, by higher chemical stability of the inorganic compounds of tin, and by lower tin recirculation speed in the biosphere.

Tin is distributed unevenly in the human environment. High tin content in certain areas and places is caused by the broad use of certain positive properties of tin, very suitable for technological procedures. Large quantities of tin are used in electrical engineering, for surface treatment of iron sheets and in canneries. The results of research indicate that the biggest source whence tin comes to the organism is victuals, especially canned goods, stewed fruit, vegetables and juices. Although tin-coated sheets are provided with organic varnishes, to protect food products against direct contact with tin, the technological shortcoming of production, inferior quality of the varnishes or excessive storage periods may often result in direct contact between aggressive victuals and the tin-coated surfaces, causing rapid corrosion of the latter.

Other possible sources of tin contamination are exhausts containing tin released during various technological procedures taking place at high temperatures. In such environments without perfect air engineering, the concentrations of tin vapours may reach considerable values, although no tin or its alloys and compounds are used directly in these operations. Tin gets into the human organism in this case by the inhalation of tin fumes and through secondary contamination of foodstuffs and objects exposed to condensed tin fumes prior to consumption.

## Acknowledgement

Our thanks are due to Ing. A. Nerudová, CSc and J. Kolbáková for the technical documentation. We should thank Dr. J. Smrčková for the mathematical analysis, and to Z. Bajer, Dr. T. Výška and Dr. J. Hrbatý for their help in taking the samples.

## References

- JAMBOR J., 1988, *Changes in Bones of Prehistoric Population Caused by Environmental Influence*, *Anthropologie* XXVI/1, 55-60
- ERICSON J.E., D.H. SHIRAHATA, C.C. PATTERSON, 1979, *Skeletal Concentrations of Lead in Ancient Peruvians*, *N. Engl. J. Med.* 300, 946-951
- PATTERSON C.C., D.H. SHIRAHATA, J.E., ERICSON, 1987, *Lead in Ancient Human Bones and its Relevance to Historical Developments of Social Problems with Lead*, *Sci. Total Environ.* 61, 167-200
- SCHROEDER, H.A., J.J. BALASSA, I.H. TIPTON, 1964, *J. Chronic Dis.* 17, 483
- SCHWARZ K., D.B. MILNE, E. VINYARD, 1970, *Biochem. Biophys. Res. Commun.* 40, 22
- UNDERWOOD E.J., 1977 *Trace Elements in Human and Animal Nutrition*. Academic Press, New York, San Francisco, London, 449-451
- WHO, 1982, *Evaluation of Certain Food Additives and Contaminants*. WHO Technical Report Series 683, Geneva 1982, 32

## Streszczenie

Zawartość cyny w kościach ludzkich badano na 149 szkieletach datowanych na I-V w.n.e., oraz 11 pochodzących ze współczesnych populacji. Kości zwęglono, a następnie poddano analizie spektroskopowej. Zawartość cyny w kościach współczesnych ludzi, nie wystawianych na kontakt z tym pierwiastkiem, jest o 1 rząd wielkości wyższa w porównaniu z kośćmi datowanymi na początek naszej ery. Artykuł omawia rozmieszczenie cyny w kościach długich w zależności od wieku osobników, a także źródła tego pierwiastka i jego rolę w procesach kontaminacji środowiskowej.