The purpose of the study was dating of the Nuraghi skeletal tissue with the use of electron paramagnetic resonance technique based on the phenomenon of the interaction of both cosmic rays and natural radioactivity of the soil surrounding the remains with bone mineral. The interaction results in the formation of a very stable radical ion $\text{Co}^{+}$ (time constant at $37^\circ$C equal to $1.9 \times 10^5$ years) giving a rise in EPR to a very specific asymmetric singlet. The intensity of the signal is proportional to the absorbed dose. The advantage of the present dating procedure was that in the close vicinity of Nuraghi tomb the Roman skeletons of the known age were also discovered. Thus, it was possible by applying the additive dose method (successive irradiation of samples at the same dose of $^{60}$Co gamma rays) to Nuraghi and Roman remains to construct plots, which by extrapolation gave values of the total cumulated doses in both samples. The dose cumulated in the Nuraghi remains was found to be equal to 31.0 Gy, while that cumulated in the Roman skeleton - 16.7 Gy. By a rather simple comparative calculation based on the assumption that the age of the Roman remains was, as established by archaeologists equal to 1700 years, the age of nuragic remains was evaluated as being equal to 3200 years (1200 years BC). The total error of the EPR measurements, EPR signal analyses and dose extrapolation was estimated to be 12-15%.

The crystallinity of the bone mineral in Nuraghi skeletons evaluated by the EPR technique, the method adapted earlier by some of the authors for biomedical studies on mineralised tissues, is only little changed after centuries of the deposition of Nuraghi remains in tombs, as compared with contemporary bone samples. This is an additional argument for the correctness of the EPR method adapted for the dating.

Comparison of the chemical composition of Nuraghi skeletons contaminated through percolation by rain or floods with that of contemporary bone shows an increase in the concentration of Fe, $\text{SiO}_2$, Al and Ca. As expected, the contamination is minimal in tooth enamel. More details on the subject one can find elsewhere [1].

References


THE CELLULOSE MEMBRANE - WATER INTERACTION STUDIED BY DIFFERENTIAL SCANNING CALORIMETRY

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Membrane processes are involved in nuclear technologies and other industries. Separation of various media on cellulose membranes is possible due to an interaction of the material of these dense membranes with solvents.

At present, the preliminary studies of cellulose membrane - water interaction were carried out applying differential scanning calorimetry (DSC). The processes like melting and crystallization of water as well as melting of the polymer phase containing...
water were examined. The studies were performed with an initial membrane material tomofoan (regenerated cellulose, product of Poland). The water content, equal to 8.82% (as related to dry polymer mass), in the film kept in air was found by thermogravimetry. Besides, two parts of the tomofoan membrane, used before as a filtration material in experiments with water, were examined. These two samples were cut from the central part of the membrane or from its edge. The first sample was exposed to the action of water at a temperature of up to 90°C and a transmembrane pressure of ca. 0.1 MPa, while the second one was subjected to the temperature treatment (up to 90°C). Moreover, some DSC measurements of initial tomofoan exposed to D2O were performed.

Melting-crystallization processes in the temperature range from -40 to +10°C were examined in heating-cooling-heating cycles at a heating-cooling rate of 1 °C/min (2 or 3 heating cycles were applied) for the moisture containing films closed in standard DSC pans. Moreover, DSC measurements for the hermetically closed samples were carried out in the temperature range 10-250°C at a heating rate of 5 °C/min. A Perkin-Elmer DSC instrument (Pyris) installed in VUB was used.

One to three thermal effects of water melting were observed during the first, second and third heating of various samples, depending on the water content, treatment time and sample history. These phenomena occur at lower temperatures than the pure water melting (Fig.1). This is due to the presence of various types of water, connected to the films with different forces. Moreover, a large amount of non-freezable water was detected, amounting to 30-50% of dry mass content. Although an extremely rapid swelling was detected by the DMTA method immediately after the sample was placed into water, the structural changes occurring in membranes as a result of the prolonged water treatment may be still concluded on the basis of both the differences between water melting occurring in particular samples, and on the appearance of the endothermal effect of melting of the crystallised polymer fraction in the temperature region 65-135°C. This effect was ob-

![Fig.1. Examples of the DSC curves, obtained during first heating: pure H2O (as calculated per 0.112 mg, while 0.670 mg was used in experiment) as well as the tomofoan film kept in water for 1 min (recorded after cooling at a rate of 1 °C/min) and for 15 min (recorded after fast cooling at a rate of 100 °C/min). Both films were dried with a paper before closing in DSC pans. The measurements were done directly after preparation. The values of the enthalpy of water melting, equal to 32.23 and 44.24 J/g, were found in the case of film exposed to water for 1 and 15 min, corresponding to ca. 10.74 and 14.76% of freezable water content, respectively. The enthalpy of pure water melting is equal to ca. 300 J/g.](image1)

**Fig.1.** Examples of the DSC curves, obtained during first heating: pure H2O (as calculated per 0.112 mg, while 0.670 mg was used in experiment) as well as the tomofoan film kept in water for 1 min (recorded after cooling at a rate of 1 °C/min) and for 15 min (recorded after fast cooling at a rate of 100 °C/min). Both films were dried with a paper before closing in DSC pans. The measurements were done directly after preparation. The values of the enthalpy of water melting, equal to 32.23 and 44.24 J/g, were found in the case of film exposed to water for 1 and 15 min, corresponding to ca. 10.74 and 14.76% of freezable water content, respectively. The enthalpy of pure water melting is equal to ca. 300 J/g.

![Fig.2. Examples of the DSC curves recorded during first heating of the tomofoan sample closed in a DSC pan with the following amount of water: 91.78 (curve 1) and 107.43% (curve 2) (ca. 75% and ca. 90% of the initial film mass, respectively). Both measurements were done after 15 h. In the case of the first sample the determined enthalpy of water melting was equal to 136.44 J/g. 45.48 and 46.30% of the freezable and nonfreezable water, respectively, was found on the basis of the above result.](image2)

**Fig.2.** Examples of the DSC curves recorded during first heating of the tomofoan sample closed in a DSC pan with the following amount of water: 91.78 (curve 1) and 107.43% (curve 2) (ca. 75% and ca. 90% of the initial film mass, respectively). Both measurements were done after 15 h. In the case of the first sample the determined enthalpy of water melting was equal to 136.44 J/g. 45.48 and 46.30% of the freezable and nonfreezable water, respectively, was found on the basis of the above result.

For the sample exposed to water for as long as 18 h, while no such effect was noticed after a short treatment time of 15 min.

Beside the influence of sample history on the further polymer-water interaction, the differences may be deduced between the H2O and D2O effect on the tomofoan membrane on the basis of the preliminary data.

Examples of the DSC curves are presented in Figs. 1 and 2. All the values of enthalpy and water content given in the captions were calculated in the term of dry mass content.