

THERMOANALYTICAL STUDY OF HUMAN BONE REMAINS

by

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The thermal decomposition of substance is characteristic to its physical and chemical structure.

The systematic observation of the thermal decomposition — named thermal analysis — is a sensitive method of analytical chemistry and research on the materials. [1]

The material complexity of bones: the simultaneous existence of organic and inorganic components was the reason to extend the field of thermal analysis by the study of bones. [3]

Today commercial thermoanalytical instruments are already available with easy handling and especially the derivatograph is remarkable [2] since it measures the following data in the very same sample, simultaneously.

Fig. 1 shows the derivatogramm of a 0,300 gramm sample of powdered bone from the year of 1931. The heating rate was 10 C°/min. The derivatogramm consists three curves, all belonging to the same temperature axis: as a function of temperature. The lower one (TG) represents the weight-loss of the sample, the intermediate one (DTG) shows the rate of the weight-loss, the upper one (DTA) characterises the heat formation in, or absorbed by the sample; this manner, by the DTA curve it is possible to indicate thermal effects without weight change (for example: melting, depolymerising, etc.)

The derivatograph — as is evident from Fig. 1. — is suitable for simultaneous recording of variations in enthalpy and weight of the substance caused by thermal effects, in the function of the sample's temperature. An advantage of the instrument is that these variations can be measured in the same sample, and beside that also the rate of weight variations is recorded (DTG curve) by the automatic derivation of the weight (TG) curve obtained in the course of the measurement. With the aid of the derivative thermogravimetric (DTG) curve, processes going on in the sample and often partly overlapping each other can be observed separately, because the frequently very slight inflexions of the TG curve appear as peaks on the DTG curve. Consequently, the results can be evaluated more easily, and moreover, their evaluation is possible sometimes only in this manner.

It can be seen from Fig. 1. — especially by the DTG curve that the thermal decomposition of the bone, below 600 C° consists three well separated processes that is: the decomposition has a stepwise character. On the basis of other thermal studies and only between the limits of the present discussion, we may assume, that in the above mentioned, below 600 C° in three processes forthcoming thermal decomposition also involves the decomposition of the organic components of the bone.

Since the quality and state of organic components of the bones appears to be in a more exact correlation with the ageing processes of the bones in the soil as the inorganic ones, the following discussion is restricted on the thermal effects only of temperatures lower than 600 C°.

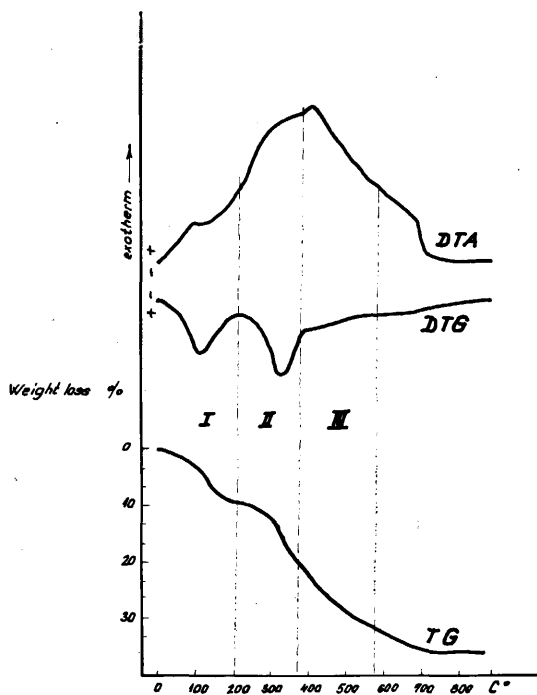


Fig. 1.

In Fig. 1 the DTG curve shows that the Process I. reaches its rate maximum at 120 C° and its end at 220 C°. On the basis of the DTA curve Process I. appears to have endothermic character, since the curve has a slight peak in the endothermic (negative) direction at 120 C°.

The beginning of Process II. is marked at 220 C° by the end of Process I. appearing on the DTG curve. The rate maximum of Process II. is at 330 C° and the end is at 380 C°. Process III. does not seem so significant beside Processes II. and I.: as from the DTG curve it is clear. The beginning of Process III. is at 380 C°, the end seems to be in the region of 580°. However the DTA curve shows a defined exothermic (in positive direction oriented) peak in the section of Process III., corresponding with the known combustibility of the bones.

Limits of the processes projected from DTG curve onto the TG curve have marked on the ordinate of the TG curve weight decreases which belong to the processes. In this way it is possible the quantitative evaluation of the derivatorgramm and of the process briefly mentioned above.

As it is known, the organic components of bones undergo a slow decomposition by time and in the soil: it appears to be a really so called material ageing process. Since the obtained weight decrease is a characteristic of the aged substance i. e.: bone, that stands in a direct relationship with chemical transformations proceeding during the ageing, investigation of this can give a deeper insight into the kinetics of the ageing processes and can develop the dating methods of bones.

On the basis of this concept derivatographic analyses was made on several bones with known but different origin and age. (The dating of these samples followed the conventional methods familiar in the archaeology.)

Origin of the studied bones and the quantitative results of the corresponding derivatograms are summarised in the following Table and in Fig. 2. It is to be remarked that the derivatograms of the different bones having similar character, differences only in the weight decreases were observed and a tendency: that the longer the time of ageing (i. e. the greater the absolute age) the simpler the derivatograms are.

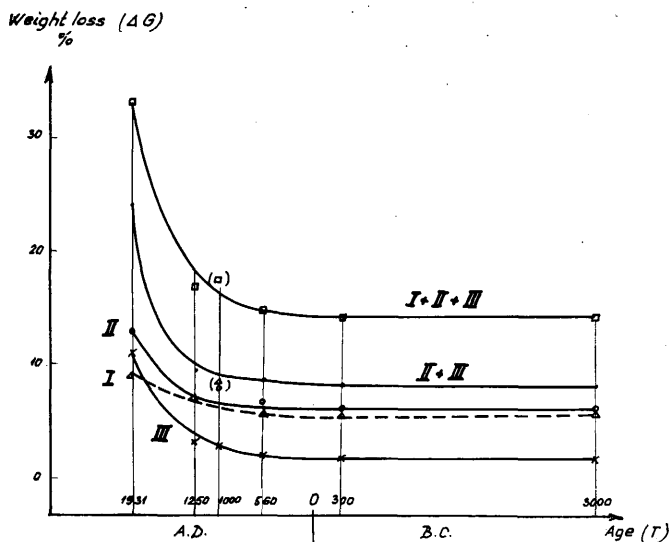


Fig. 2.

Sample		Measured weight loss % (ΔG)					Total weight loss I, + II, + III. 20 - 380 C°
year of origin	absolute age years	measured amount/gramms	Sectional processes				
			I. 20 - 220 C°	I. 220 - 380 C°	III. 380 - 580 C°	II. + III. 220 - 580 B°	
1931	0	0,300	9,16	13,0	11,3	24,0	33,20
1250	681	0,300	7,33	6,67	3,0	9,68	17,0
1000	931	0,300	8,5	8,0	2,67	9,17	1,767
550	1381	0,300	6,0	6,75	2,00	8,92	14,9
B.C. 300	2231	0,300	5,84	6,25	1,75	8,17	14,0
B.C. 3000	4931	0,300	6,17	6,17	2,00	8,17	14,3

It is to be seen, that the total weight decrease of the bone is approximately proportional to the reciprocal age and the slope of the line is in relationship with the rate of degradation processes of human bone in the soil. The formula of the straight line is

$$\Delta G = 2,84 \cdot 10^3 \frac{1}{T} + 13,4 \quad [\%]$$

where studying the limits of validity of the above formula it is clear, that the value of $1/T$ is limited, since the fresh bone also has a finite, cca 30% weight decrease (ΔG) determining by this way the maximal value of T . Therefore $T_{\min} \approx 170$ years, (consequently the sample from the year of 1931 is not represented in Fig. 3.) The validity of the above formula has also a limit in the other direction: with greater T values the first part of the formula approaches to zero and than ΔG approaches to 13,4%. Naturally the same linear interpretation is also possible of other curves (I, II and III) of Fig. 2. yielding similar straight lines which differs from each other only in their slopes and relative positions. But for the sake of brief description, it must now neglect the linear interpretation of these sectional processes.

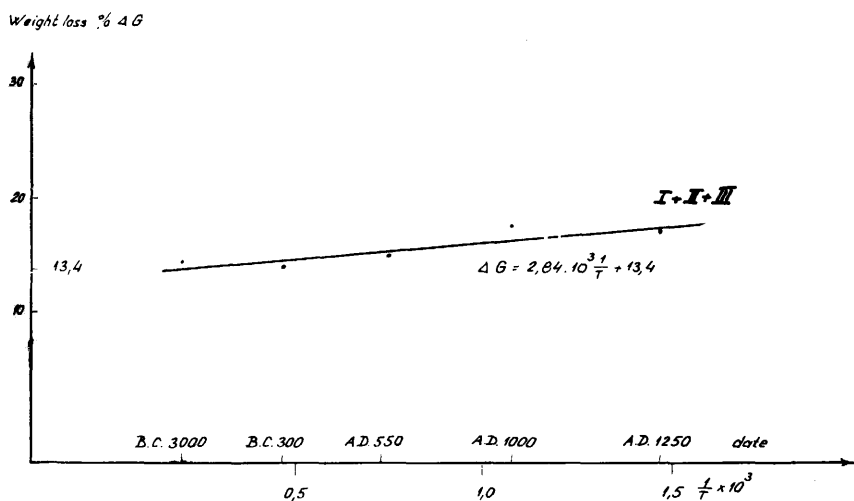


Fig. 3.

The Fig. 2. shows the weight decreases of the corresponding sectional-processes (I., II. and III.) as the function of the absolute age (T) of the studied bones. It is to be seen, that each of weight decrease curves are approaching an asymptotic value and the slopes of this curves are significant only in the time interval of the first thousand years.

With regard to the shape of the curves it appeared to be correct to choose $1/T$ coordinates instead T coordinates on the time axis of Fig. 2. This way, the total weight decrease values of Processes I+II+III (see Table) was plotted versus $1/T$, i. e. the reciprocal age. In this interpretation the function weight decrease — age shows a linear character and gives a straight line in Fig. 3.

This preliminary work does not meet all the requirements necessary for establishing a new method of dating human bones, but it can be a basis in the developing of a such dating method. Further the clear validity of the relationship discussed above should have to be remarked in contrary to the very different sorts of soil in which these were.

Acknowledgements

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References:

- ¹ Paulik, F.—Paulik, J.: *Termoanalizis*, Budapest, 1963.
- ² Erdey, L.—Paulik, F.—Paulik, J.: *Acta Akad. Sci. Hung. Chem.* 7. (1955) 55.
Paulik, F.—Paulik, J.—Erdey, L., *Z. Anal. chem.* 160. 1958) 241.
Paulik, F.—Paulik, J.—Erdey, L., *Z. Anal. chem.* 160. 1958) 321.
- ³ Dávid, P., *Elektrotechnika*, 57. (1964) 570