THERMAL ANALYSIS OF DENTAL CALCULI AND DUCT CALCULI

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There are very few papers known in the literature on thermal analysis of substances of biological origin. The study of such kind of materials is rather difficult, because the quantity of the sample is very small in most of the cases, the possibility to reproduce the analysis is limited, and samples contain organic and inorganic substances together.

In spite of that, Hungarian authors succeeded in applying thermoanalytical methods to analyse such kind of materials as nephroliths [1—3] or sclerotic aortae [4—5].

This paper reports on studying thermal decomposition of dental calculi and duct calculi using "derivatography" [6] together with other instrumental analytical methods.

In the practice of dentistry it may be important to know exactly the composition of dental calculi and duct calculi, because these data can only help to prevent the formation of such calculi or to remove chemically the calculi already formed.

Several papers have been published during the last decade on analysis of components in dental calculi. One of the authors determined the ratio of organic to inorganic content in the calculus and found 20 : 80. Moreover, the determination of the amino acid, nitrogen, carbon and ash content in the organic part has also been reported [7]. The inorganic material has been studied by X-ray diffraction methods [8, 9], neutron and gamma-ray spectrometry and by different volumetric and gravimetric methods.

In the Derivatograph the temperature of the sample rises continuously, it causes the sample to decompose at temperatures characteristic of its composition. From the decomposition temperature and the change in the sample weight the quality (from the former) and the quantity (from the latter) of components can be determined.

Materials and methods

The samples (dental and duct calculi) were carefully rinsed with distilled water, dried by pumping air through them, then pulverised in an agate mortar. Calculi have been taken from more than one patient in most of the cases, so the samples can be regarded as good averages. The calculi were divided into two main groups: as taken from patients under and over 30 years, respectively.

The equipment used in our measurements included "Derivatograph" (System F. Paulik—J. Paulik—L. Erdey), X-ray apparatus (Type Mikrometa), spectrograph (Type ZQ-119) and an infrared spectrophotometer (Type Zeiss UR-10). Determinations on "Derivatograph" consisted in weighing about 50—100 mg of the sample into the platinum crucible of the apparatus, and heating at a rate of 10 °C/min, to highest temperature of 900 °C. During the measurements normal atmosphere (air) was kept over the samples.

Results and discussion

The derivatogram *a* in Fig. 1 was taken with pulverized dental calculi of patients under age 30 as a sample. For sake of comparison, derivatogram *b* presents the thermal decomposition curve of calcium dihydrogen phosphate dihydrate ($CaHPO_4 \cdot 2\ H_2O$). Upon heating, the crystal water is liberated first, with maximal rate at 180 °C. The weight loss of the sample corresponds to the

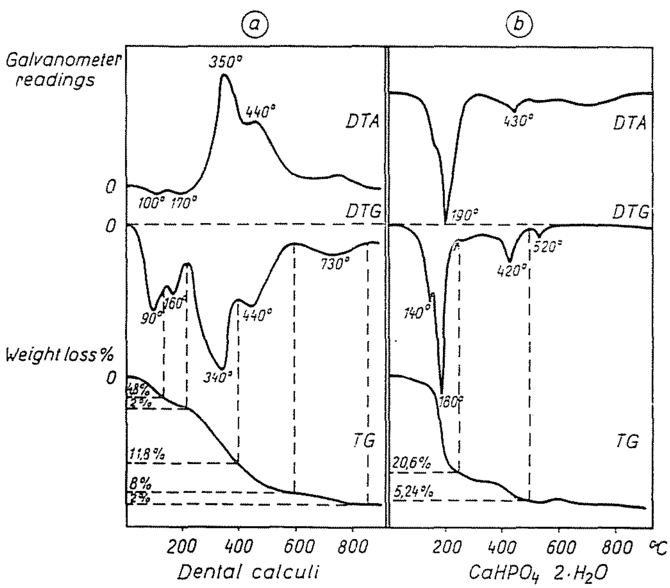

Fig. 1

stoichiometrically calculated value. At 420 °C calcium pyrophosphate is formed according to the following equation:

$$2\ CaHPO_4 \rightarrow Ca_2P_2O_7 + H_2O$$

The weight loss at the temperature mentioned is nearly stoichiometric again; water escapes, as can be seen from the above formula. There is another peak on the DTG curve at 520 °C: it corresponds to decomposition of the small calcium hydroxide content in the sample. The DTG peak at 90 °C on the derivatogram of dental calculi shows the vaporization of the water adsorbed, the maximum 160 °C is caused by the loss of the crystal water from calcium dihydrogen phosphate dihydrate. At 220 °C the organic part (the so-called matrix of dental calculus) starts to decompose, the rate of decomposition is maximal at 340 °C. As to the enthalpy changes during analysis, the liberation of water is endothermic, the decomposition is exothermic as it can be seen on the DTA curve of the derivatogram. At 440 °C calcium pyrophosphate is abruptly formed from the calcium dihydrogen phosphate along with water loss, according to the above-mentioned formula.

Rising the temperature further, in the range of 700 to 800 °C the small quantity of calcium carbonate decomposes, as it can be seen on the curves. The weight loss of the sample is 28.6% up to 900 °C; it originates from deliberation of adsorption water, crystal water and reaction water, and decomposition of the organic material.

Examining the residue by X-ray diffraction method, the presence of calcium pyrophosphate could be demonstrated, while in the original sample strong lines of $CaHPO_4 \cdot 2\ H_2O$ appeared. The residue has also been analysed by

Table I

Principal components	Samples			
	1	2	3	4
	(Ca, Mg, P) %	(Ca, Mg, P) %	(Ca, Mg, P) %	(Ca, Mg, P) %
Na	0.8 —3	0.8 —3	0.8 —3	0.8 —3
Al	0.05 —0.1	0.05 —0.1	0.05 —0.1	0.05 —0.1
Si	0.05 —0.1	0.03 —0.08	0.05 —0.1	0.03 —0.08
Fe	0.05 —0.1	0.05 —0.1	0.08 —0.3	0.08 —0.3
Mn	0.005—0.01	0.005—0.01	0.005—0.01	0.001 —0.005
Sn	0.1 —0.5	0.05 —0.1	0.05 —0.1	0.05 —0.1
Pb	0.08 —0.3	0.03 —0.08	0.08 —0.3	0.08 —0.3
Ag	0.1 —0.5	0.1 —0.5	0.1 —0.5	0.1 —0.5
Au	0.001—0.005	0.001—0.005	0.001—0.005	0.0005—0.001

spectrography; Table I shows the results of the semiquantitative analysis. The data in Table I give informations about the trace components in the sample.

The derivatogram of the average sample from patients above age 30 is given in Fig. 2. After vaporization of the adsorbed water, a DTG peak at 170 °C can be seen; it corresponds to calcium hydrogen phosphate dihydrate.

Decomposition of the organic content is shown as a peak on the DTG curve at 290 °C, and as the corresponding exotherm DTA peak with a tailing up to 470 °C.

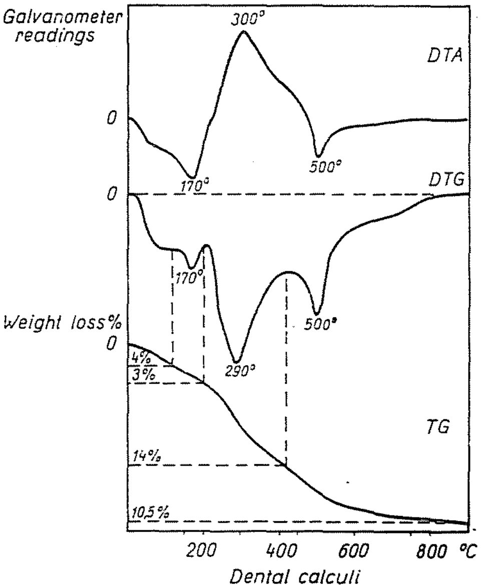

Fig. 2

In addition to decomposition of the organic substances a change in the sample's weight also appears in this temperature range: the tricalcium phosphate hydrate and the hydroxyl apatite decompose and water is produced in the process. The rate of change in weight is maximal at 500 °C.

Our results given by the thermal decomposition curves are well confirmed by X-ray diffraction tests: some calcium pyrophosphate could be found in the residue while its bulk has been shown as apatite. Another analysis by infrared spectroscopy serves as a further evidence of the above statements.

Our studies made by distinguishing between samples according to the age of the donors verified the observation of BAMBAUER [8] stating the role of patients' age in the composition of dental calculi. According to our measurements it seems that in the early period of formation the bulk of dental calculi is $CaHPO_4$, which is converted later into an apatite structure. BIDLÓ et al. [11] made quite an analogue observation: during the development of human bones similar processes take place.

Two derivatograms are given in Fig. 3: one of an average sample from duct calculi, taken from several patients (Curve *a*), and that of a single duct calculus (Curve *b*). The origin of the latter is a patient 67 years old. After the adsorbed water has evaporated, the matrix material starts to decompose over 200 °C; this process is completed at about 680 °C. Inorganic components also decompose in this temperature range and lose their structural water. There is no peak on the DTG curve at 170 °C, characteristic to calcium hydrogen phosphate. In accordance with that, no presence of calcium hydrogen phosphate or of calcium pyrophosphate could be demonstrated either in the original sample or in the residue.

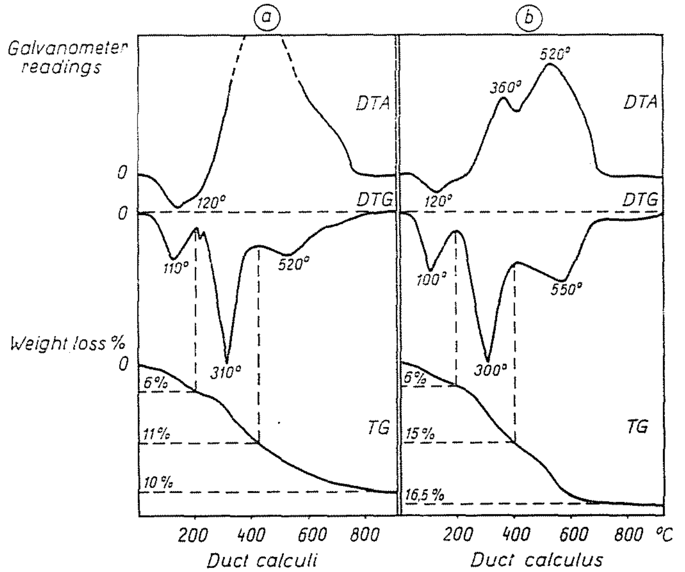

Fig. 3

The peak on the curve at 550 °C refers to the apatitic structure.

In Table II the semiquantitative composition of the duct calculus is given. The analysis was made by spectrography.

On the basis of the derivatograms shown and of other instrumental analyses it can be stated that all dental calculi are composed of the same compounds, except the organic part of the material. Only the quantitative results are different for the samples of different origin.

The composition of the analysed duct calculi is similar to the dental calculi; except that no calcium hydrogen phosphate can be detected in the samples.

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Table II

Principal components	Samples (Ca, Mg, P) %
Na	0.1 —0.5
Cu	0.001 —0.005
Ag	0.0005—0.0001
Sn	0.01 —0.05
Pb	0.01 —0.05
Fe	0.01 —0.05
Si	0.01 —0.05
Al	0.001 —0.005
Mn	0.0005—0.001

Summary

Thermal decomposition of dental and duct calculi has been studied by means of a derivatograph.

In the apatite structure of dental calculi, taken from patients under 30 years, calcium hydrogen phosphate dihydrate could be detected.

The results of thermal analysis have been substantiated by X-ray diffraction analysis, infrared spectrophotometry and spectrography.

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