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THERMAL DECOMPOSITION OF TOOTHPASTES AND TOOTHPOWDERS

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ABSTRACT

The thermal decomposition of 51 toothpastes and 3 toothpowders was studied using thermoanalytical methods: differential thermal analysis (DTA) and thermogravimetry (TG). The decomposition of all components contained in them was examined. The possibility has been demonstrated of employing DTA, TG and derivative TG (DTG) curves of the thermal decomposition of toothpastes and toothpowders for identifying some of the substances contained in them and for the quantitative determination of calcium carbonate, based on its decarboxylation process.

INTRODUCTION

In the last few decades, thermoanalytical methods, differential thermal analysis (DTA) and thermogravimetry (TG), have found their appropriate interdisciplinary place in science. The initial application, confined exclusively to metallurgy, mineralogy and analytical chemistry, has now been considerably extended. An increasing interest in employing thermoanalytical methods for examining pharmaceuticals [1–7], foodstuffs [8–10] and pesticides [11] is being observed. They can also be helpful in solving some problems of crime detection [12–14].

From a survey of the literature it follows that the problem of qualitative and quantitative testing of the composition of toothpastes and toothpowders has not been the subject of investigation so far.

EXPERIMENTAL

Materials

In this study 51 toothpastes and 3 toothpowders were used (manufacturers given in parentheses).

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Toothpastes of Polish manufacture: Azulenowa, Bambino, Colodent, Consul, Fosforanowa, Fluorodent, Nivea, Pollena 68, Protozon, Salodent and Salux ("Pollena-Lechia" Cosmetic Works, Poznań), Parodont ("Polfa" Pharmaceutical Works, Poznań), Herbadont, Herbena and Ziołowa ("Herbapol" Medicinal Plant Works, Pruszków).

Toothpastes of foreign manufacture: Arbat, Cheburashka, Extra, Myatnaya, S dobrym utrom, Semeynaya, Yagodka and Zhemchug ("Swoboda", Moscow, U.S.S.R.), Meri, Neopomorin, Omnodent, Pazur, Phytopomorin, Pomorin and Zefir ("Pharmachim", Sofia Bulgaria), Bis acidentol, Extra dent, Fluora and Viksadon ("Kozmetika", Bratislava, Czechoslovakia), Erilex (Slovakofarma Národný Podnik, Hlohovec, Czechoslovakia), Chlorodent 69, Red-white and Silica F ("Florena", Dresden, G.D.R.), Amodent and Aktiv amodent 4 ("Caola", Budapest, Hungary), Blendax fluor super (Blendax, Mainz, F.R.G.), Parodontax (Madaus und Co., Koeln, F.R.G.), Pepsodent (Elida-Gibbs GmbH, Hamburg, F.R.G.), Sensodyne (Block Drug Comp., Inc., Ratingen, F.R.G.), Deo-Signal and Signal mit Eukalyptus (Elida-Gibbs, Vienna, Austria), Elmex mit Aminofluor (Gaba AG, Basel, Switzerland), Vademecum fluor (Barmängen, Stockholm, Sweden), Ultrabrite (Colgate-Palmolive Co., London, Gt. Britain), Colgate (Colgate-Palmolive Co., New York, U.S.A.) and Pepsodent (Lever Brothers Co., New York, U.S.A.).

Powders for washing the teeth and for removing tartar ("Septoma" Chemical Cooperative Works, Zabki near Warsaw, Poland) and powder for Children ("Swoboda", Moscow, U.S.S.R.).

Apparatus and techniques

The thermal decomposition of toothpastes, toothpowders and their components was carried out using the OD-103 derivatograph, model 3427, 1500°C (MOM, Budapest, Hungary). All measurements were carried out under identical conditions. The 200-mg samples were heated in platinum crucibles of 9.5 mm diameter in a furnace atmosphere and under atmospheric pressure at a heating rate of 5 K min^{-1} up to the final temperature of 1173 K. α-Al_2O_3 was used as reference material. Each thermogram was recorded 3–6 times.

RESULTS AND DISCUSSION

Toothpastes are multicomponent formulations. Their main components are polishing and moisturizing agents, detergents, thickening agents, flavours, sweetening agents, preservatives and dyes [15]. Additionally, the pastes contain special ingredients, such as fluorine compounds, antibacterial substances, plaque-inhibiting agents, anti-phlogistic and hyperaemic substances, and gum desensibilizing agents.

Based on the information given by manufacturers on the packaging it has been stated that a number of toothpastes contain inorganic salts. Ciechocinek salt enters into the composition of Parodont paste. Salodent is a paste with the addition of mineral salt rich with microelements. Pazur, Salux and Zefir pastes also contain natural mineral salts. Omnodent paste performs its action by active HCO_3^-, Cl^-, SO_4^{2-}, K^+ and Na^+ ions, whereas the main components of Parodontax paste are Ems salt and baking soda in stabilized forms. Moreover, it should be mentioned that the Fosforanowa paste contains dicalcium phosphate.

Some toothpastes contain fractional amounts of free fluorine in the form of sodium monofluorophosphate. These are Aktiv amodent 4, Blendax fluor super, Colgate, Fluorodent and Ultrabrite pastes. Fluorine, without exactly defining the kind of salt in which it occurs, is also contained in Erilex, Fluora and Silica F pastes.

Pharmacognostic preparations are also present in the composition of many toothpastes. Azulenowa paste contains camomile extract and sodium sarcoside. A medicinal-herb extract consisting of arbutin and tannins, as well as menthol and essential oils are present in Herbadont paste, whereas the natural extracts of five medicinal herbs are present in Herbena paste. Natural antiseptic substances are present in Ziołowa paste. Parodontax is a paste containing, among other things, sage, camomile and mint. Signal mit Eukalyptus paste contains eucalyptus oil, and Aktiv amodent 4 paste contains a plant extract.

Cases when the manufacturer gives the full composition of the formulation are exceptional. The manufacturers of Colgate and Pepsodent (U.S.A.) pastes can be named here. These pastes contain sorbitol, water, hydrated silica, polyethylene glycol, sodium lauryl sulphate, cellulose resin and flavours, as well as sodium saccharate and benzoate. Additionally, Colgate paste contains glycerol, titanium oxide and dyes; Pepsodent (U.S.A.) paste contains aluminium oxide and dicalcium phosphate. All other manufacturers keep the composition of their formulations secret.

Analysis of the DTA, TG and derivative TG (DTG) thermal decomposition curves of products examined has shown that among the toothpastes of Polish, Russian, Bulgarian, Czechoslovakian, German and Hungarian manufacture, only Aktiv amodent 4, Bis acidentol, Colodent, Erilex, Protozon and Silica F pastes do not contain calcium carbonate. Among the pastes manufactured in the remaining states, calcium carbonate is present only in Deo-Signal, Pepsodent (F.R.G.), Signal mit Eukalyptus, Ultrabrite and Vademecum fluor pastes.

Decarboxylation of calcium carbonate occurs over the temperature range 873–1073 K. It is not disturbed by the decomposition of simple organic compounds, since they are burnt up completely at temperatures up to 873 K. In this connection the mass loss on the TG curves that reflects the release of carbon dioxide was used for the quantitative determination of calcium

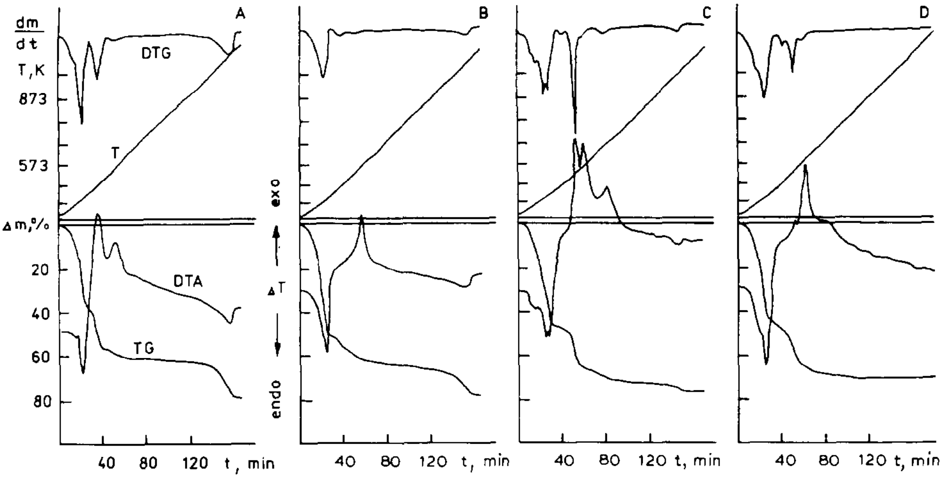

Fig. 1. DTA, TG and DTG curves of the thermal decomposition of the toothpastes: (A) Myatnaya, (B) Ziołowa, (C) Signal mit Eukalyptus and (D) Aktiv amodent 4.

carbonate content in the toothpastes analysed. DTG curves are very helpful in this case, since they allow the beginning of the decarboxylation to be determined. The characteristic shape of the DTA curves over this temperature range is one more factor confirming the proper identification of the decomposition process of calcium carbonate.

In Fig. 1A the DTA, TG and DTG curves of the thermal decomposition of Myatnaya paste are presented, that contains about 37% of calcium carbonate. This is the shape of decomposition curves typical of all toothpastes which contain calcium carbonate as their main component. Results of the determinations for these products are listed in Table 1. Analysis of the data has shown that the residue after the decomposition contains not only calcium oxide. Identification of these components is not possible based on the DTA, TG and DTG curves, however. Over the temperature range from 303 K to about 413–433 K a large percentage mass loss is observed on the TG curve, which is associated with the evaporation of the volatile components of the toothpaste. This is confirmed by the endothermic effects on the DTA curve. The DTG curve distinctly points to at least a two-stage process. It can be assumed that water, glycerol, polyethylene glycol, flavours and the pharmacognostic-material extract are liberated in this stage. This mass loss allows conclusions to be drawn on the approximate total content of the liquid components of the toothpaste.

The shape of the DTA curve over the higher temperature range yields little information, which, due to the lack of any manufacturer's data on the content of the particular components of the toothpaste, makes it impossible to describe its composition. The DTG curves indicate that the product examined undergoes a slow decomposition with no distinctly separated stages.

TABLE 1

Results of the determination of the calcium carbonate content in toothpastes

Trade name	Temp. range (K)	Weight loss (%)	Calcium carbonate content (%)	Residue in the crucible (%)	
				theor. [a]	found
Amodent	903–1088	19.6	44.6	25.0	27.2
Arbat	873–1043	15.8	35.9	20.1	23.0
Azulenowa	858–1048	17.5	39.8	22.3	26.9
Bambino	848–1038	17.4	39.6	22.2	26.1
Consul	848–1043	16.7	38.0	21.3	22.5
Cheburashka	873–1048	17.0	38.6	21.6	21.9
Extra	903–1093	16.8	38.2	21.4	23.5
Fluora	883–1053	14.0	31.8	17.8	21.6
Fluorodent	858–1053	17.1	38.9	21.8	23.9
Meri	883–1033	13.2	30.0	16.8	22.4
Myatnaya	868–1043	16.4	37.3	20.9	23.0
Nivea	853–1043	14.9	33.9	19.0	23.4
Parodont	963–1073	15.0	34.1	19.1	30.2
Pazur	873–1038	15.0	34.1	19.1	22.0
Pollena 68	863–1048	17.2	39.1	21.9	24.9
S dobrym utrom	858–1043	17.1	38.9	21.8	23.8
Semeynaya	878–1043	14.6	33.2	18.6	20.4
Ultrabrite	863–1073	18.5	42.1	23.6	27.1
Yagodka	883–1058	15.3	34.8	19.5	24.7
Zefir	848–1048	18.0	40.9	22.9	27.2
Zhemchug	853–1023	12.1	27.5	15.4	21.1

[a] Theoretical residue in the crucible was calculated as calcium oxide.

The second group are the toothpastes which also contain calcium carbonate, but the stage associated with its decarboxylation is not so distinctly marked on the DTA, TG and DTG curves as in the case of pastes listed in Table 1. This is depicted in Fig. 1B and C, where the decomposition curves of Ziołowa and Signal mit Eukalyptus pastes are presented. There can be many reasons for this conjuncture. One of them is a small content of calcium carbonate, which yields a small mass loss associated with the release of carbon dioxide. Some of these pastes contain mineral salts of undefined composition or medicinal-herb extracts, powdered medicinal herbs and other pharmacognostic preparations. Sodium phosphates, sodium bicarbonate and magnesium carbonate can undergo decomposition over the temperature range analysed. Sodium lauryl sulphate and the sodium salts of organic acids, such as benzoic acid and saccharine, also undergo decomposition. The decomposition of these substances occurs over a wide temperature range without intermediate decomposition stages being distinctly shaped. Moreover, the decomposition stages of several compounds, which proceed over close temperature ranges, overlap each other to form a resultant stage.

TABLE 2

Results of the determination of the calcium carbonate content in the toothpastes

Trade name	Temp. range (K)	Weight loss (%)	Calcium carbonate content (%)	Residue in the crucible (%)	
				theor. [a]	found
Chlorodent 69	916–1011	5.2	11.8	6.6	12.5
Deo-Signal	undeterminable				
Extra dent	893–1033	9.1	20.7	11.6	33.2
Fosforanowa	903–1028	7.6	17.3	9.7	24.2
Herbadont	883–1043	11.6	26.4	14.8	25.0
Herbena	876–1038	8.6	19.6	11.0	18.2
Neopomorin	896–1033	9.5	21.6	12.1	35.2
Omnodent	893–1093	13.5	30.7	17.2	33.0
Pepsodent (F.R.G.)	913–1003	4.9	11.1	6.2	26.5
Phytopomorin	888–1033	11.0	25.0	14.0	31.3
Pomorin	853–1013	8.2	18.6	10.4	36.8
Red-white	923–1013	7.2	16.4	9.2	13.0
Salodent	903–1013	5.2	11.8	6.6	33.6
Salux	undeterminable				
Signal mit Eukalyptus	undeterminable				
Vademecum fluor	885–1013	8.7	19.8	11.1	22.7
Viksadon	908–1033	9.2	20.9	11.7	22.2
Ziołowa	883–1038	11.0	25.0	14.0	24.0

[a] Theoretical residue in the crucible was calculated as calcium oxide.

This is accompanied on the DTA and DTG curves by single peaks that are difficult to ascribe to the presence of a definite component of the toothpaste. They also influence the decomposition of calcium carbonate and make the beginning of its decarboxylation difficult to determine. The residue after decomposition is a mixture of calcium oxide and inorganic salts, which are probably the/sulphates and carbonates not undergoing decomposition up to 1073 K.

In Table 2 the results of the determinations of calcium carbonate content in the toothpastes as characterized above are listed. It should be taken into account that in some cases the calcium carbonate content as determined may not be in agreement with its content declared by the manufacturer.

Toothpastes which do not contain calcium carbonate are the third group of products studied. They comprise most of the pastes manufactured in Western Europe. DTA, TG and DTG curves of their thermal decomposition are not characteristic. This is illustrated by Fig. 1D, in which the decomposition curves of the Aktiv amodent 4 paste are presented. Without the help of classical analytical methods it is not possible to unequivocally identify the components contained in this type of toothpaste. Components such as silica or aluminium oxide do not undergo decomposition over the temperature range analysed. The decomposition of the remaining components proceeds in accordance with the general description given above. In this connection these thermograms can only be employed for distinguishing the toothpastes from each other. They also supply information on the content of liquid components and the amount of residue after decomposition of inorganic compounds and of the salts of organic acids.

The thermal decomposition has shown that calcium carbonate is the fundamental component of toothpowders. The powder for tooth-washing contains 85% of calcium carbonate, that for children 95%, and that for tartar-removal contains the least, only 62.7% of calcium carbonate. The remaining components are inorganic salts. Some of them decompose at temperatures up to 713 K.

CONCLUSIONS

The studies carried out show some usefulness of thermoanalytical methods for the qualitative and quantitative checking of the composition of toothpastes and toothpowders. It is most advantageous to conduct the identification of particular components on the basis of simultaneously recorded DTA, TG and DTG curves of the thermal decomposition of the product under test. Use is made of the temperature ranges and the areas and shapes of particular DTA and DTG peaks as well as of corresponding mass losses on the TG curves.

For the determination of calcium carbonate content, based on its decarboxylation process, TG and DTG curves were exclusively employed. In this way its content in more than half of the formulations analysed was determined without the necessity of separating calcium carbonate from the other components of the toothpaste. The content of the remaining components was not determined for the following reasons: (a) the particular stages of the thermal decomposition of several components overlap each other, (b) the decomposition of a particular component is not characterized by distinctly separated stages, (c) some components fail to undergo any thermal changes over the temperature range under test, and (d) a significant part of the components occurs in small quantities of several per cent.

Generalizing the results of the study carried out, it can be stated that the DTA, TG and DTG methods are useful for the identification and quantitative analysis of toothpastes and toothpowders, but only when the thermal decomposition characteristics of the compounds contained in the formulation being decomposed are previously defined and catalogued. For this purpose the data on the per cent content of all components of the product under test are needed, information which is not supplied by the manufacturers. In a mixture, particularly one as complex as toothpastes and toothpowders, the particular components will always influence each other. Consequently, the thermal decomposition of the formulation will be a resultant process. In this connection one component, the presence of which is not expected in the product being decomposed and whose characteristics of thermal decomposition are in this connection not known, may remain undetected or else it will unfavourably influence the detection of the remaining compounds contained in the toothpaste or toothpowder.

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