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THERMAL STABILITY OF SELECTED SPICES

Abstract: Nowadays diets are rich of spices and herbs. These additives are used not only to improve the flavor of dishes, but also acting positively on human health. Spices change the taste and color of prepared meals, as well as acting preservative. Many spices found the application in the kitchen because of their properties. They exhibit antioxidant and antiradical properties. They are used also for changing colour and can be an important source of antioxidants and vitamins. Therefore it is particularly interesting to study effect of high temperatures that accompanied the preparation of food on properties of the spices.

Thermal stability of selected commercial spices has been investigated by means of thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) in the temperature range 20–500°C. Comparison is made between thermal stability and thermal phase transition analysis recorded for selected spices. Application of both methods can give complex and wide information about stability of spices.

In this work we present the effect of heating on several spices contained in chicken spices' mixture and all spices separately. It was found that all spices exhibit thermal stability only up to boiling temperature. Only few spices exhibit stability to frying temperature. It was also found that analysis of the TG and DSC curves for a mixture does not provide information about the composition. Therefore both methods cannot be used for identification of the components of the mixture. Practical applications of TGA and DSC methods in quality control of spices and other dry foods as well as in food processing are suggested.

Keywords: thermal stability, spices.

Introduction

Nowadays, spices and herbs can be found in almost every home and are used as an ingredient in dishes, salads, bakery products, as well as ingredients of tinctures and mortar. One can buy them at most grocery stores for a small price, in various forms and mixtures. Spices in the kitchen are used to improve flavor, aroma or color. Besides these advantages spices are used because of their positive affect the human body. Therefore, drugs, medicinal infusions or poultices often contain the extract of herbs [Babś 2011].

Herbs and spices have a traditional history of use, with strong roles in cultural heritage, and in the appreciation of food and its links to health. Demonstrating the benefits of foods by scientific means remains a challenge, particularly when compared with standards applied for assessing pharmaceutical agents [Tapsel et al. 2006]. Food is eaten in combinations, in relatively large, unmeasured quantities under highly socialized conditions. The place of herbs and spices in the diet needs to be considered in reviewing health benefits [Wieczorek 2007]. It has been identified nearly 5,000 plant's chemical substances present in spices. Many of them show antitumor activity and antiatherosclerotic. Spices can be also a significant source of antioxidants [Hozyasz & Chełchowska 2005].

Research mostly focus on identification bioactive substances in herbs and spices. They can also focus on their properties as a whole food, and/or be set in the context of a dietary cuisine. Recommendations for intakes of food do not yet include suggested intakes of herbs and spices. In addition to delivering antioxidant and other properties, herbs and spices can be used in recipes to partially or wholly replace less desirable ingredients such as salt, sugar and added saturated fat in, for example, marinades and dressings, stir-fry dishes, casseroles, soups, curries and Mediterranean-style cooking [Tapsel et al. 2006; Diplock et al. 1998; Idle 2005]. Vegetable dishes and vegetarian options may be more appetizing when prepared with herbs and spices.

Typical spice used for improving colour and flavor of chicken's meat is mixture of different spices and herbs. There are many different mixtures consisting of several spices and herbs. Typical spices used in these mixtures include nutmeg, cinnamon, clove and ginger. These spices contain two groups of chemicals, allylbenzenes and their isomers, propenylbenzenes. It was suggested that these substances act as metabolic precursors of amphetamines [Idle 2005]. Whether or not the pharmacology and toxicology of spices such as nutmeg can be explained on the basis of their allylbenzene or propenylbenzene content is speculative [Idle 2005; Heikes 1994; Shimoni et al. 2003]. Humans may be exposed to amphetamines derived from these precursors in forno, the formation during baking and cooking [Idle 2005]. However, the role of these aromatic substances, acting simply as odors, evoking old memories of winters past, cannot be ignored [Idle 2005; Shimoni et al. 2003]. Whether spices have a true pharmacological effect or they act as aromatherapy can be elucidated through clinical and laboratory studies.

The aim of our study was to investigate the thermal stability of selected commercial samples of spices usually included in mixture of spices for chicken by means of thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) in the temperature range 20–500°C.

1. Experimental

Materials

The highest quality samples of individual spices usually included in mixture of spices for chicken "Złocista" were purchased at the local supermarkets. Examined spices are: chili, nutmeg, ginger, sweet red pepper, spicy red pepper, fenugreek, cinnamon, curcuma, cumin, coriander, garlic, clove.

In each case the analysis was carried out using freshly opened sample of the spice. All samples were finely powdered in a porcelain mortar prior before the analysis.

Methods

Thermal stability of the samples was determined by means of thermogravimetric analyzer TGA-50 (Shimadzu) and differential scanning calorimetry (DSC) (Shimadzu) equipped with personal computer. All analysis of spices were carried out in the temperature range 20–500°C. The samples were analyzed in alumina crucibles using α-Al_2O_3 as a reference substance. In all analysis the heating rate of 10°C/min, and the sampling frequency of 1.0 s were applied.

2. Results and discussion

Thermal gravimetric analysis (TGA) is a simple analytical technique that measures the weight loss or weight gain of the material as a function of temperature. Changing the weight of many different chemicals with an increase in temperature is their characteristic.

As materials are heated they can loose weight from simple process such as drying, or from chemical reactions that liberate gasses. Very often weight loss is connected with disruptive processes to the sample material [Rzechuła i Pertkiewicz-Piszcz 2009]. Differential scanning calorimetry (DSC) involves heating or cooling a test sample and an inert reference under identical conditions, while recording the temperature difference between the sample and reference. DSC measures the temperatures and heat flows associated with transitions in materials as a function of time and temperature [Rzechuła & Pertkiewicz-Piszcz 2009]. These measurements provide quantitative and qualitative information about physical and chemical changes that involve endothermic or exothermic processes, or changes in heat capacity.

Mixture of spices for chicken "Złocista" consist of many spices and herbs. Figure 1 presents TG curves for "Złocista" mixture and some of mixture's components: chili, nutmeg, ginger and sweet red pepper.

As can be seen in Figure 1, decomposition of the samples of herbs and spices proceeds in several steps. The TG data analysis for all samples shows that the thermal decomposition begins at 50°C. This change is related to a decrease in mass of the samples, possibly corresponding to a loss of the most volatile fragrant compounds

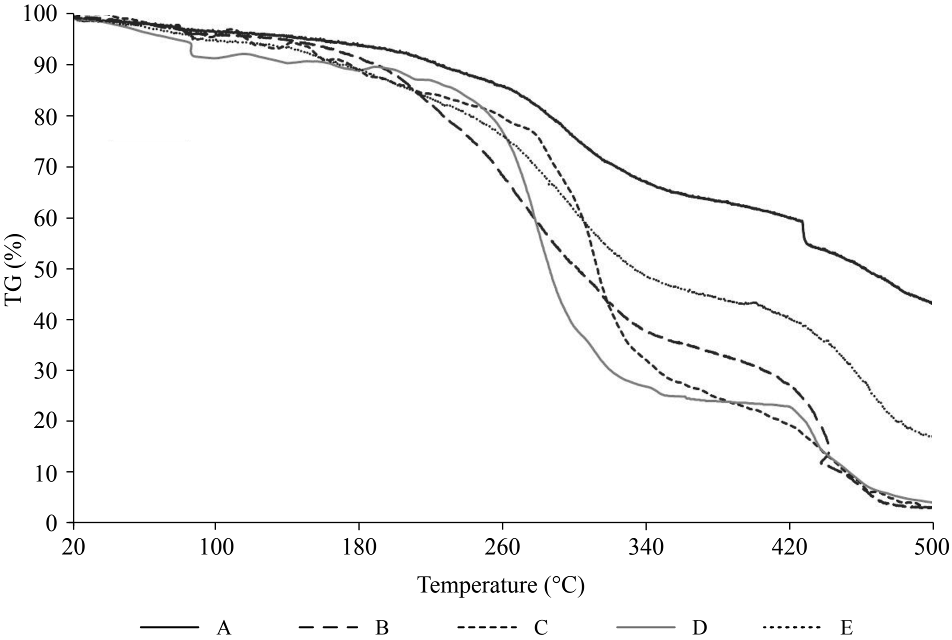

Figure 1. TG curves of: A – "Złocista", B – chili, C – nutmeg, D – ginger, E – sweet red pepper

(essential oil). After that temperature begins slight weight loss. Rapid decomposition of chili sample starts at about 180°C, nutmeg, ginger and sweet red pepper at about 220°C. That points indicate for inflection point. Over 420°C for samples B, C, D, E can be observed second inflection point.

Figure 2 shows TG curves recorded for "Złocista" mixture, spicy red pepper, fenugreek, cumin, coriander. Decomposition of all samples begins in room temperature and slight loss of weight can be observed. This loss of weight is ended by inflection point. As it can be seen in Figure 2 for samples F, G, H, I, at 240°C, one inflection point can be observed. At temperatures higher than 240°C the TG curves show rapid decomposition. The second inflection point can be observed for samples F, G, I at about, as follows, 420°C, 460°C, 400°C.

Figure 3 shows TG curves recorded of "Złocista" mixture, garlic, curcuma, clove, cinnamon. As it can be seen decomposition of the samples proceeds in several steps. TG curves recorded for samples J and M presents slight loss of weight in low temperature and one inflection point at about 180°C and 220°C. It can be also seen the thermogram recorded for curcuma has two inflection points at temperatures 220°C and 400°C. It can be seen in Figure 3 that the TG curve of clove and does not have strong inflection points, what can indicate its constant thermal decomposition. It is also important to notice that "Złocista" mixture has the smallest weight loss only to 44%. It indicates that mixture consist of ingredients that decompose over 500°C e.g. salt.

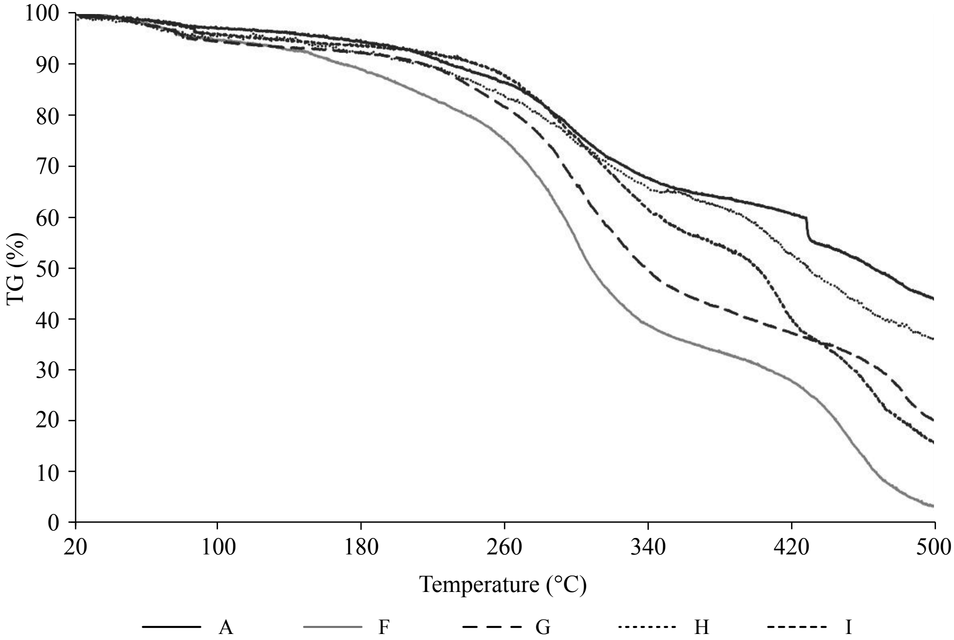

Figure 2. TG curves of: A – "Złocista", F – spicy red pepper, G – fenugreek, H – cumin, I – coriander

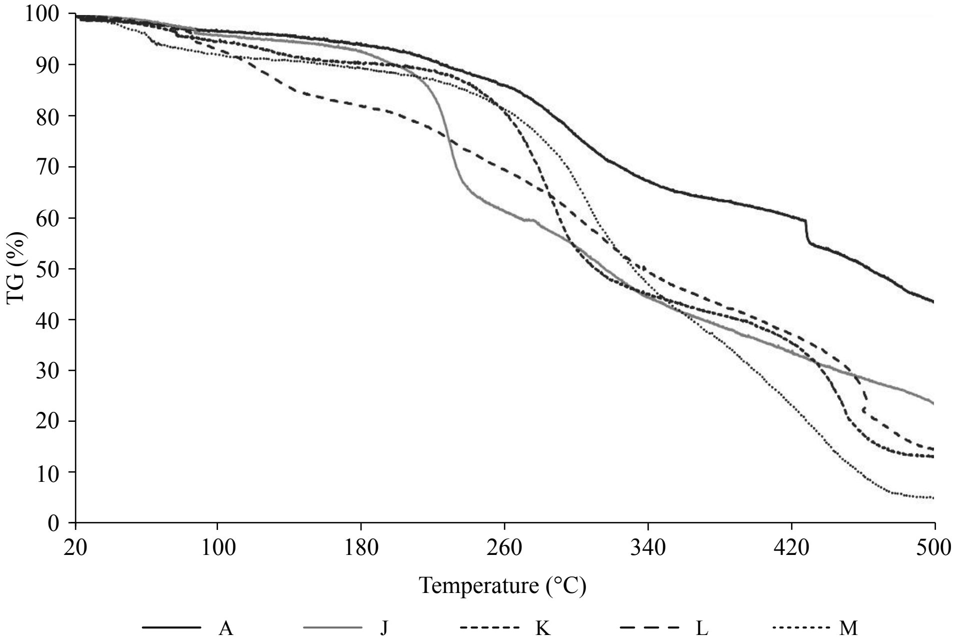

Figure 3. TG curves of: A – "Złocista", J – garlic, K – curcuma, L – clove, M – cinnamon

DSC thermograms stands as result of measurement of temperature difference between sample and reference substance. If the tested substance does not occur any changes during the analysis, the temperature of the substance and reference substance varies in the same manner in accordance with the agreed conditions of analysis. Heating elements, in which DSC is equipped provide heating to maintain a uniform temperature in the two crucibles. When the temperature of the reference substance is higher than the temperature of the sample endothermic signal can be observed. Exothermic signal is observed in opposite circumstances. DSC thermogram presents the dependence of thermal energy supplied (in mW or W/g) on the temperature (or time).

Figure 4 presents DSC curves recorded for chili, nutmeg, ginger and sweet red pepper in the temperature range of 20–500°C. For comparison, in all Figure the DSC curve recorded for "Złocista" mixture is also presented. As can be seen in Figure 4, all examined samples have 2 phase transitions. Maxima of first mild exothermic signals are located at ca 290°C for samples C, D and 320°C for samples B, E. Second exothermic signals are stronger and located at ca 440°C for samples C, D and 460°C for samples B, E. It can be noted that DSC curve recorded for "Złocista" mixture differs from other curves presented in Figure 4. It can be seen that DSC curve of the Złocista" mixture has two mild exothermic signals with maximum located at ca 335°C and 480°C. It indicates that heat and enthalpy of transitions of that sample are much lower than spices presented in Figure 4.

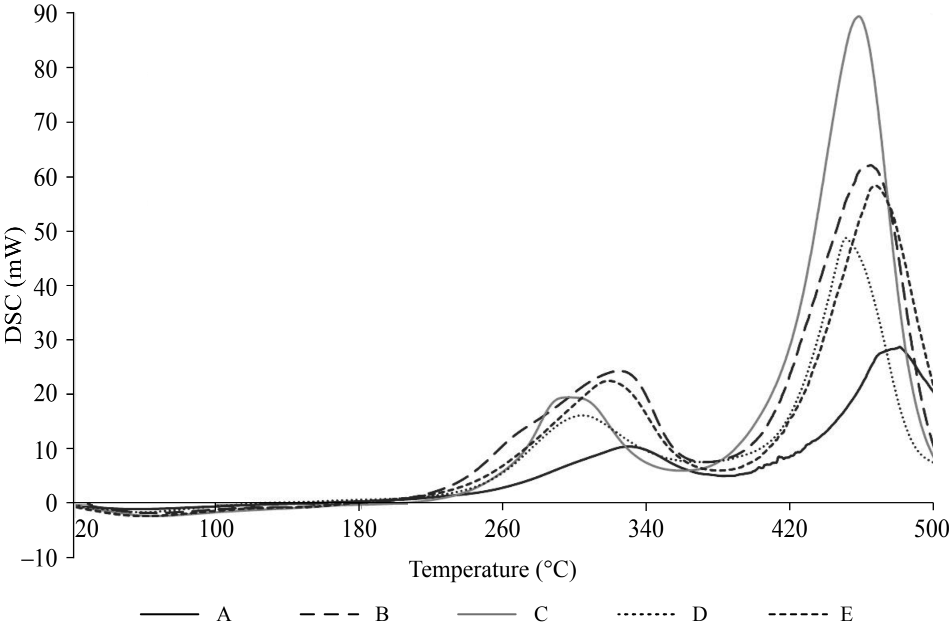

Figure 4. DSC curves of: A – "Złocista", B – chili, C – nutmeg, D – ginger, E – sweet red pepper

Figure 5 presents DSC curves recorded for “Złocista” mixture, spicy red pepper, fenugreek, cumin, coriander. DSC thermogram of spicy red pepper shows two mild exothermic signals with maximum located at ca 315°C and 465°C. Two mild and one sharp exothermic signals can be seen in DSC curve recorded for cumin. Their maxima of these phase transitions are located at ca 330°C, 415°C and 470°C.

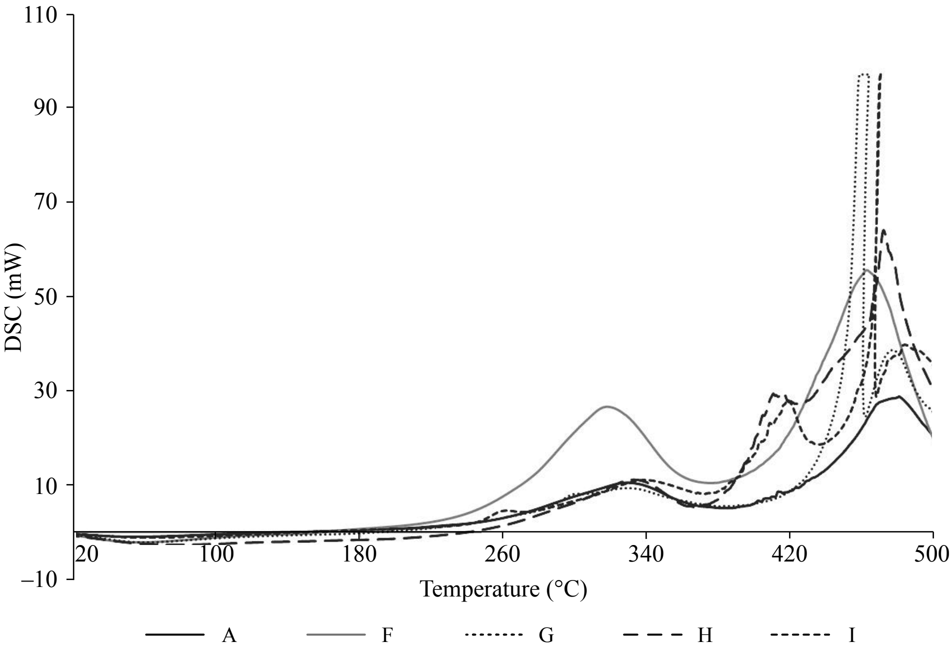

Figure 5. DSC curves of: A – “Złocista”, F – spicy red pepper, G – fenugreek, H – cumin, I – coriander

Figure 6 shows DSC curves recorded for “Złocista” mixture, garlic, curcuma, clove, cinnamon. There can be observed two mild exothermic signals at about 325°C and 435°C on the thermogram of cinnamon sample. It can be also seen two exothermic signals on the DSC curve recorded for curcuma. First signal with maximum located at about 290°C is mild and wide, second signal observed in temperature about 445°C is sharp and high. As it can be seen in DSC curve recorded for garlic sample thermogram has 3 mild exothermic signals. Their maxima are located at ca 225°C, 320°C and 430°C.

Thermogram of fenugreek (Fig. 5) has one mild and wide exothermic signal in temperature about 325°C. There can be seen three exothermic signals in temperature about 260°C, 415°C and 480°C on the coriander’s thermogram (Fig. 5).

Thermogram of clove’s sample (Fig. 6) has also signals of exothermic phase transitions. One of them is located at ca 330°C. It is mild and wide. It can be also seen that DSC curve of clove (Fig. 6), coriander and fenugreek (Fig. 5) have one

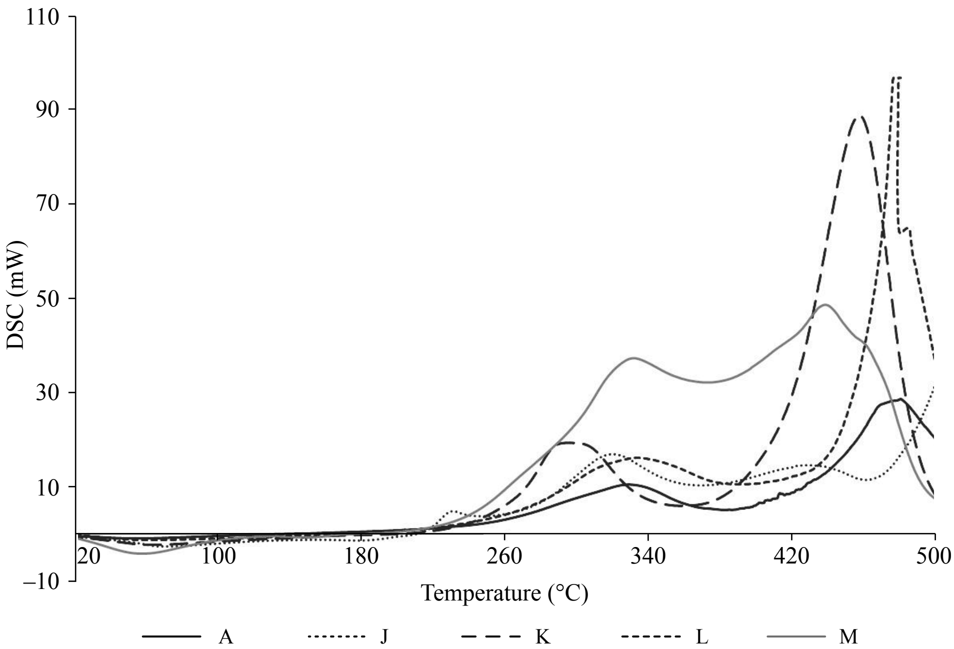

Figure 6. DSC curves of: A – "Złocista", J – garlic, K – curcuma, L – clove, M – cinnamon

very strong and sharp exothermic signal. Maximum of the signal is located, as follows, at ca 475°C, 470°C and 455°C. These signals can be attributed to a decomposition of the substances included in the spice. Top of this exothermic signal is moved to higher temperature. It indicates that during phase transition the emission of energy is so high and sudden that accelerates heating up of the system over linear temperature's increase of DSC analyzer. Precise calculation of the enthalpy of this transformations is not possible. There is also important to notice that all spices exhibit small endothermic signal in the temperature range 40–80°C.

Conclusions

The presented results of thermal analysis of selected spices included in "Złocista" mixture indicate that the tested spices are thermally stable in the temperature range 180–250°C. In all the thermograms shown weak endothermic signal at temperatures around 40–80°C, which can be attributed to the loss of most most volatile fragrant compounds.

Conducted analysis provide valuable information on thermal treatment of spiced dishes. The obtained data show that in the cooking temperature (about 100°C) all tested spices are thermally stable. At digestion, frying, and baking temperature tested spices gradually lose their thermal stability. At digestion spices are thermally stable, except for the garlic and chili, which began its decomposition at 180°C. In the frying process its thermal stability has lost most of the tested spices, except nutmeg, ginger and coriander. During baking none of the tested samples was no longer thermally stable.

In summary, the combination of presented in this article methods allows for quick and precise determination of thermal stability of spices. Such information may be valuable, because it allows to select the appropriate temperature range not only culinary but also in the process of drying and/or processes for storage of spices.

From the DSC curves of "Złocista" mixture it can not be read characteristic signal of phase transitions of components. Thus, the study shows that thermal analysis methods do not provide information about the composition of the mixture.

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STABILNOŚĆ TERMICZNA WYBRANYCH PRZYPRAW

Streszczenie: Dieta człowieka jest bogata w zioła i przyprawy. Dodatki te są wykorzystywane nie tylko do poprawy smaku, zapachu czy barwy potraw, ale również stosuje się je w celach prozdrowotnych. Dlatego szczególnie interesujące są badania wpływu wysokich temperatur, które towarzyszą przygotowaniu żywności, na właściwości przypraw.

Stabilność termiczną wybranych handlowych przyprawy badano za pomocą analizy termograwimetrycznej (TG) i skaningowej kalorymetrii różnicowej (DSC) w zakresie temperatur 20–500°C. W pracy przedstawiono porównanie wyników uzyskanych dla mieszanki przypraw do kurczaka „Złocista" z wynikami uzyskanymi dla poszczególnych jej składników indywidualnie. Stwierdzono, że wszystkie przyprawy wykazują stabilność termiczną do temperatury wrzenia wody. Tylko kilka z analizowanych przypraw wykazuje stabilność do temperatury smażenia. Stwierdzono również, że analiza krzywych TG i DSC dla mieszaniny nie dostarcza informacji o jej składzie. Dlatego też żadna z metod nie może być używana do identyfikacji składników mieszaniny.