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Thermal analysis of vitamin PP Niacin and niacinamide

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Abstract Vitamin PP includes two vitamers, niacin and niacinamide which are essential for energy production. Vitamins are sensitive and losses can occur during shelf life and heating processes. Thermal analysis can provide information about thermal behavior of each vitamer relating them with time and/or temperature exposure. The vitamers thermal behavior were studied by TG/DTG and DSC under air and nitrogen atmosphere and the results showed that niacin is more stable than the niacinamide and the decomposition happens by volatilization at 238 °C while niacinamide melts at 129 °C and volatilize at 254 °C when there is the total mass loss in the TG/DTG curves.

Keywords DSC · Niacin · Niacinamide · TG/DTG · Vitamin PP

Introduction

Vitamins are essential organic compounds for human metabolism. They are in most of the foods in low concentrations. Several compounds have vitamin activity and can be divided in two groups according to their solubility: lipossoluble vitamins (A, D, E and K) and hydrossoluble vitamins (C, B_1, B_2, B_5 or panthotenic acid, B_6, B_{12}, PP or niacin, folic acid, biotin, inositol and choline). The biological activity of each vitamin can be due to one or more compounds called vitamers [1, 2].

Vitamin PP includes two vitamers, niacin or nicotinic acid and niacinamide or nicotinamide. Both compounds have basic properties and are converted to nicotinamide adenine dinucleotides (NAD) and nicotinamide adenine dinucleotides phosphate (NADP) in the organism. NAD and NADP have essential participation in the energy production from carbohydrates, fatty acids and amino acids as well in the synthesis and repair of DNA [1, 3, 4].

High concentration of vitamin PP is found in meat, chicken, fish, vegetables and whole cereals. In this kind of food, about 85% of the vitamin is bounded to polysaccharides and peptides and are not bioavailable [1, 3, 4].

Most of the vitamins are extremely sensitive and its stability is influenced by many factors like temperature, moisture, oxygen, light and pH. The vitamin losses can occur during food or product shelf life and processing steps mainly thermal treatments [3].

Niacin and niacinamide have similar molecular weigh (123.11 and 122.12, respectively), are odorless and transparent needle shape. The melting point for niacin is within 235–237 °C and for niacinamide, 130–133 °C [4]. The structural formulas of all these compounds are showed on Fig. 1.

Many steps of food processing can lead to thermal degradation of vitamins due to exposition to high temperature. The thermal analysis can provide information about thermal behavior of each vitamer relating them with time and/or temperature exposure. Thermal analysis is a group of analytical techniques that can measure physical properties of a sample and/or their reaction products submitted to a controlled program of temperature [5].

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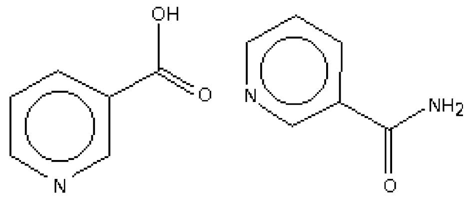

Niacine Niacinamide

Fig. 1 Structural formulas of niacin and niacinamide

Thermogravimetry/derivative thermogravimetry (TG/DTG) and differential scanning calorimetry (DSC) are used together to provide information that can characterize substances like thermal stability, melting point, phase transitions and thermal decomposition [6].

TG/DTG results show mass variation against time or temperature giving information about composition and thermal stability of the sample, intermediate products and formed residues [5]. The kinetics studies of isothermal and non-isothermal events can provide the parameters such as activation energy, frequency factor and shelf life. DSC can detect events related or not to mass losses, indicate the substance purity from the fusion endothermic phenomenon [7].

Thermoanalyical techniques have been used to characterize drugs and interaction among formulation compounds. The thermal stability study of drugs and information related to storage effects due to temperature and time can be obtained. So, the use of TG/DTG and DSC can provide relevant information about thermal stability of the vitamins, possible interactions among them and the behavior in a complex matrix as food [8–11].

When a sample is submitted to a controlled program of temperature there is a variation in the sample mass. This variation is showed in a TG/DTG curves ad the DSC curves give information about first order transitions (enthalpy) and second order transitions (calorific capacity). The analysis of both curves provides information about the compound fusion, loss of mass, desorption and reduction reactions.

The objective of this paper was to study the thermal behavior of the vitamin PP vitamers, niacin and niacinamide by TG/DTG and DSC.

Experimental

Materials

Analytical standard of niacin and niacinamide from Merck were used. The standards were kept in dissecator cabinet during the study to avoid moisture absorption.

Thermogravimetry/derivative thermogravimetry (TG/DTG)

TG/DTG curves for the vitamers were obtained in a Shimadzu thermobalance, model TGA-50, under air and nitrogen atmosphere (50 mL/min), using platinum crucible, heating rate of 10 °C/min and samples mass of approximately 5 mg [12].

Differential scanning calorimetry (DSC)

The DSC curves were obtained using a Shimadzu DSC-50 cell under nitrogen atmosphere (50 mL/min), in the temperature range from 25 to 550 °C using a heating rate of 10 °C/min and aluminum crucible partially closed using about 2 mg of sample. The cell was calibrated and/or verified for temperature before the analyses using as standards Indium (T_{fusion} = 156.6 °C) and zinc (T_{fusion} = 419.5 °C), both standards with 99.9% of purity. It was used the metallic Indium fusion ΔH to determine the heat quantity (28.71 J/g) [12].

Results and discussion

Figures 2 and 3 show the TG/DTG and DSC curves for niacin and niacinamide under N_2 atmosphere, inside of

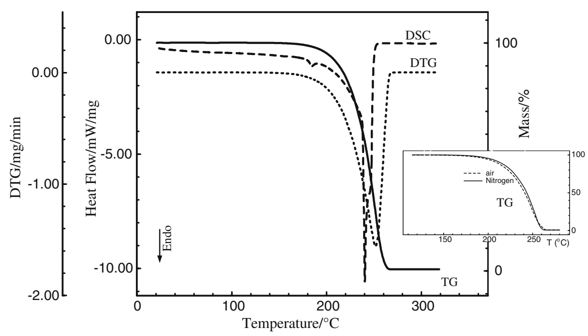

Fig. 2 TG/DTG and DSC curves obtained at 10 °C/min and under N_2 atmosphere for niacin

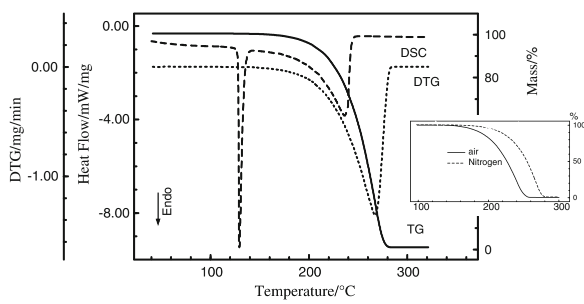

Fig. 3 TG/DTG and DSC curves obtained at 10 °C/min and under N_2 atmosphere for niacinamide

figures there is the overlap of TG curves obtained in air and N_2 atmosphere.

The thermal behavior of niacin is showed by the TG/DTG and DSC curves in the Fig. 2. The compound is thermally stable until 235 °C approximately and has a unique event of total mass loss (peak temperature = 276 °C) in the TG/DTG curves. The DSC curve shows the sample melting at 238 °C. The overlapping of TG curves obtained under air atmosphere and N_2 show the same thermal behavior in both atmospheres, indicating and confirming the volatilization of the material.

Figure 3 shows the TG/DTG and DSC curves for niacinamide. It is possible to visualize an endothermic in the DSC curve between 125 and 140 °C (peak temperature = 129 °C) characterizing the material fusion because the TG/DTG curves showed no mass loss at this temperature range. From 140 and 260 °C there is another endothermic (peak temperature = 236 °C) that can be due to the material volatilization. The TG/DTG curves showed a mass loss in a unique event similar to volatilization (peak temperature DTG = 254 °C).

Figures 4, 5, 6, 7, 8 and 9 show the curves and graphs registered and constructed during the cinetic triplet

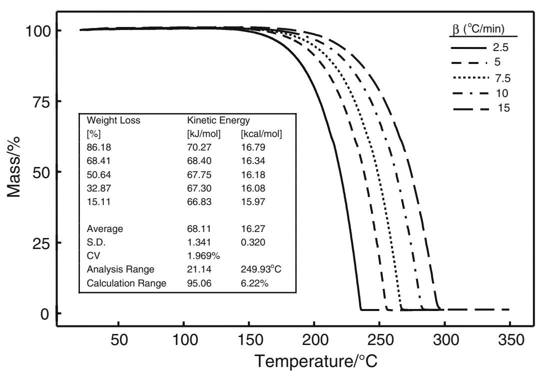

Fig. 4 TG curves obtained under air dynamic atmosphere and different heating rate (β) of niacinamide sample

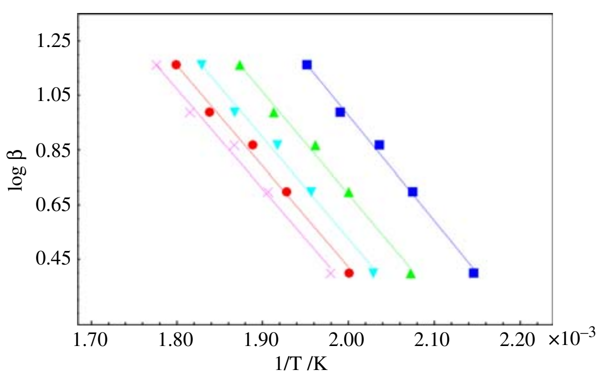

Fig. 5 Graph of the logarithm of the heating rate (β) in function of the inversion of the temperature constructed from TG curves

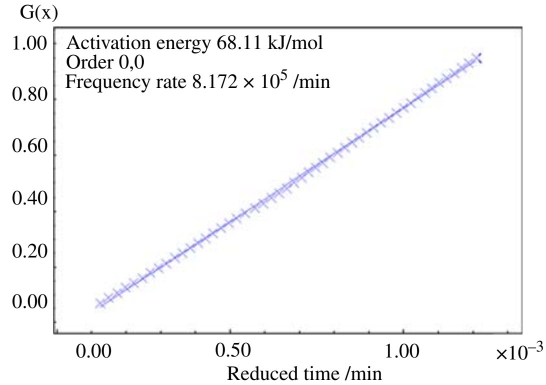

Fig. 6 Graph of the function G(x) of the inverse of the temperature for niacianamide

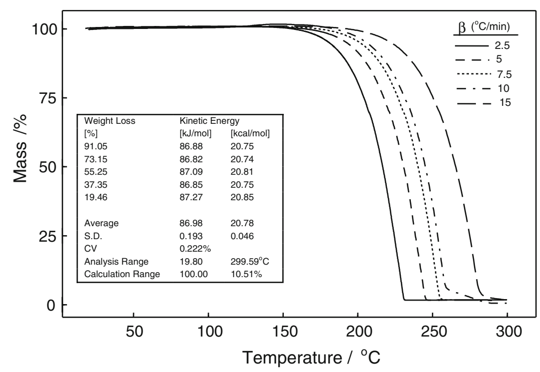

Fig. 7 TG curves obtained under air dynamic atmosphere and different heating rate (β) of niacin sample

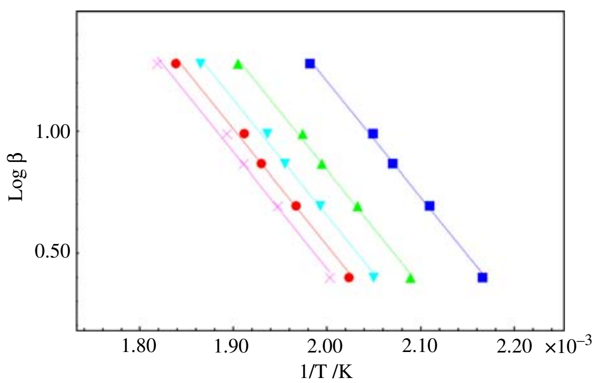

Fig. 8 Graph of the logarithm of the heating ratio (β) in function of the inverse of the temperature constructed from TG curves

obtention process, using the model proposed by OZAWA in accordance with the kinetic analysis program developed by Shimadzu for the two vitamers (niacinamide and niacine). Data were obtained from heating the samples until 250–350 °C in the heating rates of 2.5; 5.0; 7.5; 10 and 15 °C/min, at air dynamic atmosphere. The curves for determination of

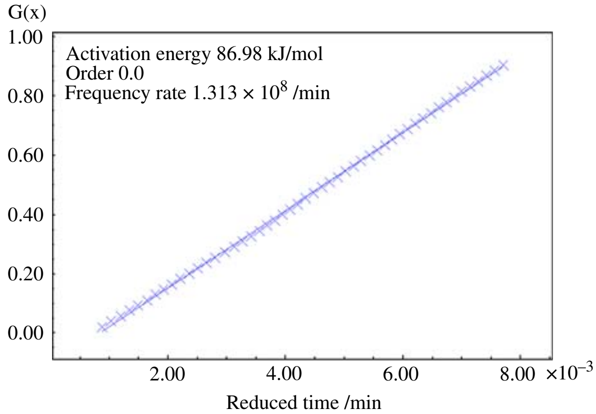

Fig. 9 Graph of the function G(x) of the inverse of the temperature for niacine

activation energy for niacinamide and niacine, has a logarithmic relation between heating rate and the inversion of the temperature. This turns possible to obtain the conversions for the decomposition phenomenon of the samples. The reaction mechanism is defined by the relationship between sample residual mass for the reduced time.

The obtained results showed that the activation energy values for samples volatilization of niacinamide and niacine, were 66 and 86 kJ/mol respectively, indication that it is necessary to give a larger amount of heat to initiate the process for the two samples. The purpose for this phenomenon related wit the melting process suggest an order zero reaction for the two vitamers, as in this situation the experimental values showed a better correlation with the theoretical curve.

Conclusions

The TG/DTG and DSC curves for niacin and niacinamide show different thermal behavior for the compounds. Niacin is more stable than niacinamide and the decomposition happens by volatilization at 238 °C while niacinamide melts at 129 °C and volatilize at 254 °C when there is the total mass loss in the TG/DTG curves.

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References

1. Ball G. Bioavailability and analysis of vitamins in foods. 1st ed. London: Chapman & Hall; 1998.
2. Bobbio F, Bobbio P. Introdução à química de alimentos. 2a.ed. São Paulo: Varela; 1989.
3. Ottaway PB. The technology of vitamins in food. 1st ed. London: Blackie Academic & Professional; 1993.
4. Sant'ana HMP. Niacina. In: Penteado MVC, editor. Vitaminas: aspectos nutricionais, bioquímicos, clínicos e analíticos. Barueri: Manole; 2003. p. 331–59.
5. Wendlandt WW. Thermal analysis. 3rd ed. New York: Willey; 1986.
6. Matos JR, Machado LDB. Análise térmica – termogravimetria. In: Canevarolo SV, Jr., editor. Técnicas de caracterização de polímeros. São Paulo: Artliber Editora Ltda; 2004. p. 209–28.
7. Machado LDB, Matos JR. Análise térmica diferencial e calorimetria exploratória diferencial. In: Canevarolo SV, Jr., editor. Técnicas de caracterização de polímeros. São Paulo: Artliber Editora Ltda; 2004. p. 229–61.
8. Araújo AAS, Storpirtis S, Mercuri LP, Carvalho FMS, Santos Filho M, Matos JR. Thermal analysis of the antiretroviral zidovudine (AZT) and evaluation of the compatibility with excipients used in solid dosage forms. Int J Pharm. 2003;260:303–14.
9. Ford JL, Timmins P. Pharmaceutical thermal analysis. Technique and applications. NewYork: Willey-Intersc; 1986.
10. Giron D. Contribution of thermal methods and related techniques to the rational development of pharmaceuticals—part 1. Pharm Sci Technol Today. 1998;1(5):191–9.
11. Giron D. Contribution of thermal methods and related techniques to the rational development of pharmaceuticals—part 2. Pharm Sci Technol Today. 1998;1(6):262–8.
12. Felsner ML. Caracterização de méis monoflorais de eucalipto e laranja do Estado de São Paulo por técnicas termoanalíticas. PhD Thesis, University of São Paulo, São Paulo, Brazil; 2001.