

Identification of Products of Thermal Decomposition in Sweetener Using Dynamic TG and Pyrolyzer Coupled to GC/MS

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Abstract: The thermogravimetric profile of sweetener, Aspartame (APM) and 5-Benzyl-3,6-dioxo-2-piperazineacetic acid (5BZ) standards presented six, four and one events of thermal decomposition, respectively. In sweetener and APM have occurred dehydration and volatilization of methanol, which was confirmed stoichiometrically. The Py-GC-MS results of APM and sweetener indicated volatilization of methanol and Phenylalanine Methyl Ester (PME), which were identified as products of thermal decomposition. The product PME was common at APM and 5BZ standards suggesting the conversion of APM to 5BZ. In sweetener occurred formation of PME by degradation process similar to APM.

Key words: Sweetener, thermogravimetry, Py-GC-MS, APM, PME

INTRODUCTION

Besides of use as dietetic products, the artificial sweeteners are used in medicines for mask organoleptic characteristics and products of buccal hygiene to decrease incidence of caries, because artificial sweeteners are not metabolized by bacteria generally found in the mouth (Lehniger, 1990). Aspartame is an artificial sweetener that was discovered accidentally in United States by Schlatter in 1965 (Fatibello *et al.*, 1996).

The kinetic factors, temperature and time, provoke the decomposition of components, with formation of new compounds that can be noxious to the health, demonstrating the importance of the study of food products (Wendlandt, 1986; Carrasco, 1993).

Thermal analysis constitutes a group of techniques of great interest for the characterization of foodstuffs, as it relates relevant foodstuffs data to the industrial process, decreasing analysis time and the sample quantity required for obtaining the kinetic parameters (Wendlandt, 1986; Carrasco, 1993).

Thermogravimetry is a thermal analytical technique by which the variation in mass is measured as a function of temperature or of time. This technique has been applied with great success not only in chemistry but also in other areas such as foods, ceramics, metallurgy and

pharmacology (Medeiros *et al.*, 2002; Botelho *et al.*, 2002; Conceicao *et al.*, 2002; Souza and Macedo, 1997; Tavares *et al.*, 2002).

The combination of Pyrolyzer coupled to Gaseous Chromatography tandem Mass Spectrometry allows the analyst to examine a much wider range of materials and it can be used to identify volatile products in foodstuffs (Fortes and Baugh, 1999). In this research had been identified the products of thermal decomposition in sweetener contain aspartame as sweetening agent using Dynamic Thermogravimetry (TG) and Pyrolyzer coupled to GC/MS. Then was performed study kinetic of process.

MATERIALS AND METHODS

The samples of the sweetener, containing aspartame as sweetening agent, were acquired in the Brazilian local market. The sweetener composition is: 38% of aspartame; 57.02% of lactose (diluent); 2.4% of carboxymethylcellulose sodium (disintegrating agent); 1.5% of polyvinylpyrrolidone (agglutinant); 0.8% of silicon dioxide (antiumectant) and 0.28% of magnesium stearate (lubricant).

The aspartame and 5-benzyl-3,6-dioxo-2-piperazineacetic acid (5BZ) standards were acquired in Merck and Aldrich, respectively.

Thermogravimetric measurements: The dynamic thermogravimetric curves were obtained in TGA-50 Shimadzu Thermobalance, sample mass of 5 mg, under air atmosphere, flux of 20 mL min⁻¹, heating rates of 10, 15 and 20 °Cmin⁻¹ up to 500 °C.

Pyrolyzer measurements: The samples were heated in Shimadzu Pyrolyzer coupled to Shimadzu Gas Chromatograph tandem Mass Spectrometer, Helium atmosphere, flow of 1.2 mL min⁻¹, column 30 m x 0.25 mm. The Py-GC-MS of sweetener, aspartame and 5-benzyl-3,6-dioxo-2-piperazineacetic acid (5BZ) standards were performed at 190, 200 and 240 °C, respectively and mass spectrum were compared in the Wiley Library.

Kinetic study: The kinetic study was undertaken for the stage that represents the beginning of the thermal decomposition process of the samples. This study was performed by the dynamic method and it corresponds to the determination of the probable reaction mechanism and of the kinetic parameters: Order of Reaction (n), Apparent Energy Activation (E_a) and Pre-Exponential Factor (A).

The determination of the mechanism that describes the thermal decomposition reactions of the samples, using dynamic thermogravimetric curves, was undertaken using the g(α) function and the Coats and Redfern (1964) method. In order to determine the kinetic parameters reaction order (n), apparent activation energy (E_a) and pre-exponential factor (A), the Coats and Redfern (1964), Madhusudan *et al.* (1963), Horowitz and Metzger (1964) and Van Krevelen *et al.* (1951) equations were fed into the Determination Program of Kinetic Parameters for the range of decomposed fractions (α) from 0.10-0.90.

RESULTS AND DISCUSSION

The thermogravimetric profile of sweetener, aspartame and 5-benzyl-3,6-dioxo-2-piperazineacetic acid

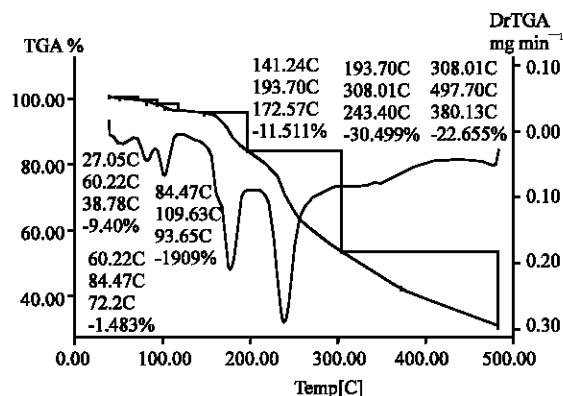


Fig. 1: TG/DTG curves of sweetener

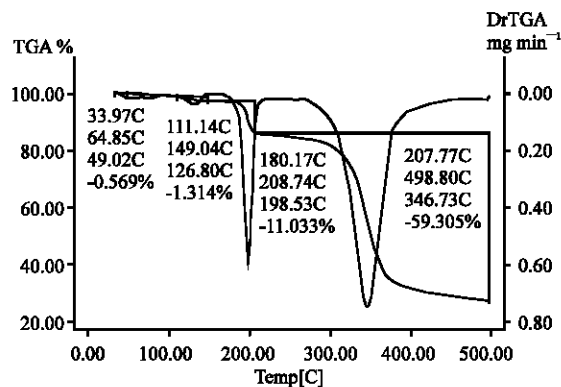


Fig. 2: TG/DTG curves of aspartame standard

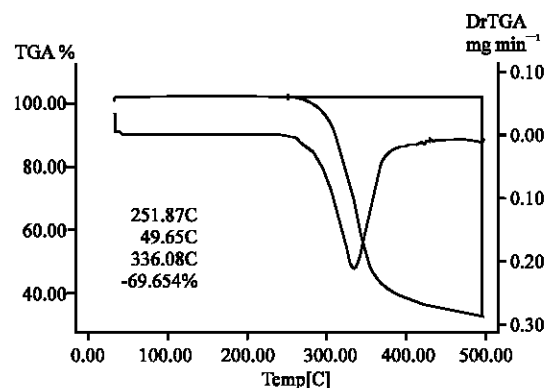


Fig. 3: TG/DTG curves of 5BZ standard

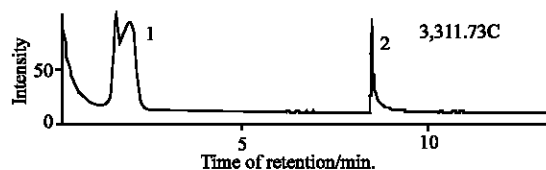


Fig. 4: Chromatogram of aspartame standard

standards presented 6, 4 and 1 events of thermal decomposition, respectively (Fig. 1-3). In sweetener and aspartame have occurred dehydration (up to 109°C and up to 149°C), volatilization of methanol (141-193°C and 180-208°C), which was confirmed stoichiometrically and decomposition process (193-497°C and 208-498°C). In 5-benzyl-3,6-dioxo-2-piperazineacetic acid occurred decomposition process (251-494°C).

The decomposition temperatures of aspartame, 5-benzyl-3,6-dioxo-2-piperazineacetic acid and sweetener obtained by thermogravimetric profiles were important in Py-GC-MS analyses application.

The Py-GC-MS showed that aspartame presented two peaks at 2 and 8.5 min corresponding volatilization of methanol and phenylalanine methyl ester, which were identified as products of thermal decomposition (Fig. 4).

Table 1 Kinetic parameters of aspartame thermal decomposition

Kinetic model	Kinetic parameters	Heating rates $10^{\circ}\text{C}.\text{min}^{-1}$	$15^{\circ}\text{C}.\text{min}^{-1}$	$20^{\circ}\text{C}.\text{min}^{-1}$
Coats - Redfem	n	0.08	0.04	0.02
	E [kJ.mol ⁻¹]	343	325	316
	A [s ⁻¹]	2.32 E+36	2.15 E+36	2.03 E+35
	r	0.99995	0.9999	0.9997
Madhusudanan	n	0.03	0.00	0.00
	E [kJ.mol ⁻¹]	339	314	302
	A [s ⁻¹]	7.51 E+35	2.33 E+35	6.78 E+34
	r	0.9999	0.9997	0.9996
Horowitz - Metzger	n	0.00	0.00	0.00
	E [kJ.mol ⁻¹]	351	348	341
	A [s ⁻¹]	1.26 E+37	7.54 E+36	4.22 E+36
	r	0.9993	0.9986	0.9992
Van Krevelen	n	0.05	0.03	0.00
	E [kJ.mol ⁻¹]	346	340	335
	A [s ⁻¹]	2.80 E+38	9.45 E+37	2.65 E+36
	r	0.9845	0.9645	0.9581

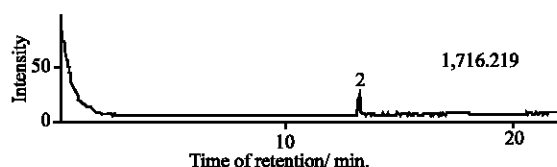


Fig. 5: Chromatogram of 5BZ standard



Fig. 6: Chromatogram of sweetener

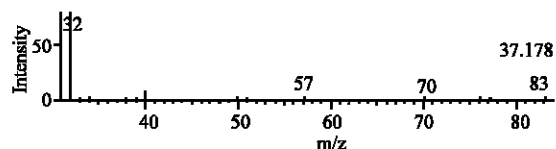


Fig. 7: Mass Spectrum of peak 1 of sweetener

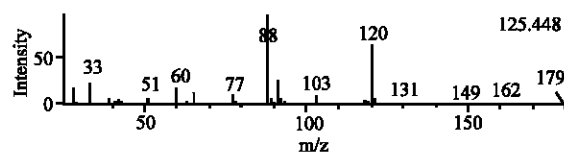


Fig. 8: Mass Spectrum of peak 2 of sweetener

The 5-benzyl-3,6-dioxo-2-piperazineacetic acid presented peak corresponding at phenylalanine methyl ester at 12 min (Fig. 5).

The sweetener presented two peaks at 2 and 8.5 min (Fig. 6-8) similar to aspartame standard.

The Py-GC-MS showed that aspartame presented two peaks at 2 and 8.5 min corresponding volatilization of

methanol and phenylalanine methyl ester, which were identified as products of thermal decomposition.

Therefore the decomposition product phenylalanine methyl ester was common at aspartame and 5-benzyl-3,6-dioxo-2-piperazineacetic acid standards suggesting the conversion of APM to 5BZ. In sweetener occurred formation of phenylalanine methyl ester by degradation process similar to aspartame.

The sweetener presented other peaks attributed at degradation of the excipients: Lactose and magnesium stearate (Fig. 6).

Kinetic study: The kinetic study of the thermal decomposition of aspartame and of the sweetener, which comprises the determination of the probable mechanism and the kinetic parameters, was undertaken for the stage corresponding to the beginning of the thermal decomposition of the samples.

For the beginning of the thermal decomposition of the samples, the model that best fitted, in other words that presented the best linear correlation coefficient, the experimental data of all the samples and all the three heating rates used for aspartame (third stage) was the kinetic model R1, related to the boundary layer zero order reaction. As for the sweetener (fourth stage) was chosen the kinetic model F1, related to a first order nucleation process.

The kinetic parameters determined by the dynamic method were: reaction order (n), activation energy (E_a) and pre-exponential factor (A). These kinetic parameters, for the beginning of the thermal decomposition of the samples, were determined as previously described and are presented in Table 1 and 2.

The different heating rates used yielded the same mechanism, varying the values of the kinetic parameters. It was observed that the activation energy progressively decreases when the heating rate used is raised, because the higher the rate of a reaction, the smaller will be the spent energy. The kinetic parameters obtained by the

Table 2 Kinetic parameters of the thermal decomposition of the sweetener

Kinetic model	Kinetic parameters	Heating rates 10°C.min ⁻¹	15°C.min ⁻¹	20°C.min ⁻¹
Coats-Redfern	n	1.38	1.14	1.06
	E [kJmol ⁻¹]	160	157	140
	A [s ⁻¹]	8.15 E+16	7.37 E+15	6.25 E+15
	r	0.9983	0.9985	0.9984
Madhusudanan	n	1.33	1.28	1.15
	E [kJmol ⁻¹]	157	145	143
	A [s ⁻¹]	3.94 E+16	2.15 E+16	2.71 E+16
	r	0.9984	0.9987	0.9984
Horowitz-Metzger	n	1.48	1.36	1.23
	E [kJmol ⁻¹]	176	171	163
	A [s ⁻¹]	6.36 E+18	4.69 E+17	3.80 E+17
	r	0.9984	0.9984	0.9983
Van Krevelen	n	1.53	1.47	1.31
	E [kJmol ⁻¹]	168	165	151
	A [s ⁻¹]	1.56 E+23	1.45 E+23	8.08 E+22
	r	0.9824	0.9815	0.9861

integral methods and by the approximation methods presented a good agreement and they were satisfactory. The values obtained by the approximation methods were bigger than the values obtained by the integral methods, what is due to the different mathematical treatments of each method.

CONCLUSION

The thermal decomposition products of samples, methanol and phenylalanine methyl ester, suggested by Thermogravimetry were confirmed for Py-GC-MS, which has differentiated the degradation pathway of aspartame and 5BZ by converted products.

In the event corresponding to the beginning of the thermal decomposition of the samples, the kinetic model that best fitted the dynamic experimental data, for all the samples and for all the heating rates was the kinetic model R1 (zero order) for aspartame. For the sweetener, the best adjustment refers to the kinetic model F1 (first order). The best fitting corresponds to the best linear regression coefficient.

The techniques of Thermogravimetry and Py-GC-MS have shown as a powerful tool to identify decomposition products of complex substances.

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