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THERMAL BEHAVIOUR OF SOME INDUSTRIAL AND FOOD DYES

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Thermal behavior of four food dyes, i.e. tartrazine, crysoine, azorubine and amarant was studied under non-isothermal conditions, in dynamic air atmosphere and at heating rates of 5, 10, 15 and 20°C min^{-1}. The TG data were correlated to the FTIR spectra of each sample, before and after the thermal decomposition. Kinetic study by processing the TG data was performed. The main conclusion of this study is that the non-parametric kinetic method allows a separation of the steps of a complex process and that the values of the activation energy obtained by this method agree satisfactory with that of Flynn–Wall–Ozawa estimation.

Keywords: *azo-dyes, food dyes, non-isothermal kinetics*

Introduction

In the last years the thermal analysis is more and more used for food safety [1]. A relative new trend in this field is the kinetic analysis of the thermal degradation of food additives [2, 3].

The aim of the present work is to study the thermal behavior under non-isothermal conditions of four derivatives used as food dyes. This thermal behavior will be characterized by means of a kinetic analysis completed with an analysis of the FTIR spectra before and after the thermal decomposition.

The studied compounds were the ones presented in Fig. 1.

These additives are used by tinned food, yoghurt, jam, in doses between 20–300 mg kg^{-1}. In order to protect the customers, it is of a real interest to know and/or to be able to simulate the thermal behavior of such food additives, taking into account that by food processing the temperature can reach 350°C.

Experimental

Synthesis

In order to avoid any possible mixture and contamination by some commercial products, the studied compounds were carefully synthesized by the classical diazo route, in basic solution and temperature below 5°C.

Thermal analysis

The thermoanalytical data were obtained on a PerkinElmer DIAMOND TG-DTG device, using Al crucibles. The experiments were performed in nitrogen, respectively air dynamic atmosphere (100 mL min^{-1}), at four heating rates, β: 5, 10, 15 and 20°C min^{-1}.

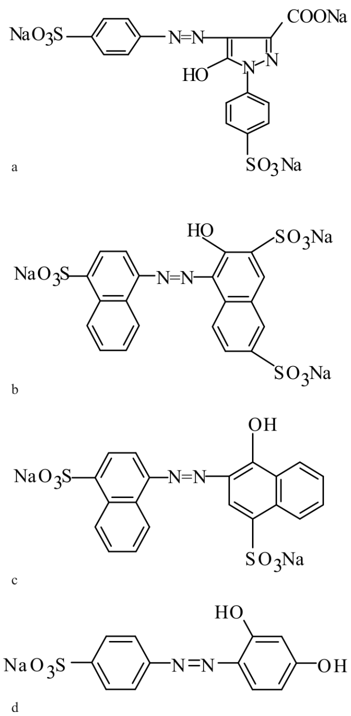

Fig. 1 Chemical structures of the studied compounds:
a – Tartrazine (E102) yellow; b – Amarant (E123) red;
c – Azorubine (E122) red; d – Crysoine (E 103) yellow

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FTIR spectra

The spectra corresponding to the samples before and after the thermal decomposition were recorded on a PerkinElmer Spectrum 100 device using the U-ATR technique.

Results and discussion

Thermoanalytical data

All the four compounds proved a high thermal stability in nitrogen, i.e. nothing is observed on the TG curves till 600°C. Although a food processing under nitrogen atmosphere is very seldom, however the data in nitrogen attest on the intrinsic thermal stability of thus structure.

Under dynamic air atmosphere the thermal behavior is quite different, like that presented in Fig. 2.

Some of the relevant data for the thermal stability are systematized in Table 1.

Widely the most stable compound is Tartrazine: a 3% mass loss at 400°C assure a suitable safety border by thermal processing of any food. In an opposite situation are Azorubine and Amarant: the decomposition process begins yet at 150–175°C. Moreover, Amarant is deeply destroyed (more than 30 mass% between 150 and 220°C).

By inspecting Table 1, two observations are important for our proposed kinetic study:

- the bad separation of the steps should create some difficulties by the kinetic analysis;
- the low mass loss along a large temperature range should generate difficulties by data processing of Azorubine, therefore this data will not be included in the kinetic analysis.

FTIR data

In order to obtain more information about what is happening during the thermal decomposition, comparative FTIR spectra before and after the thermal degradation were drawn up and presented in Fig. 3.

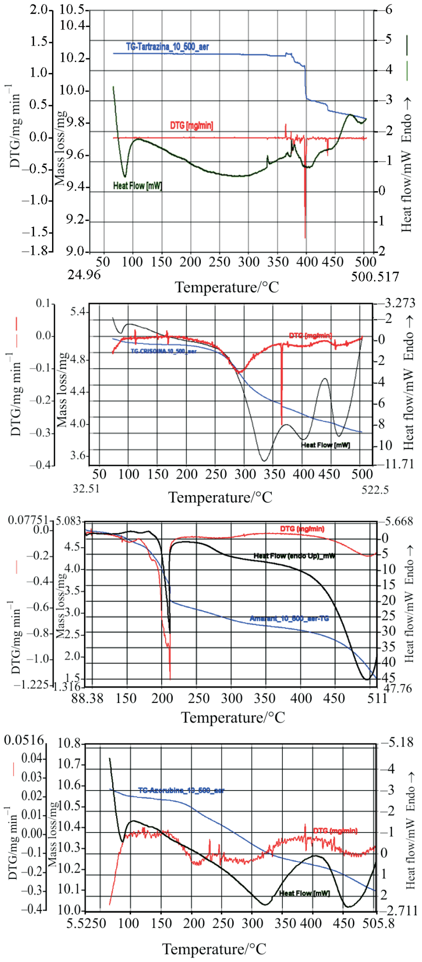

Fig. 2 The TG/DTG/HF curves in air flow at β=10°C min^{-1}

By a first inspection, it is remarkable a significant simplification of the spectra in the range of 1600–700 cm^{-1}, a range containing almost all characteristic wave number. In connection with the data in Table 1, the greatest qualitative change corresponds to Amarant, the compound with the greatest mass loss during the thermal decomposition.

Table 1 Characteristics of thermal behavior in air

Compound	Decomp. step	Beginning T_i/°C	End T_f/°C	Max. rate T_{max}/°C	Heat flow	Mass loss/%	Obs.
Tartrazine	1	400	400	400	Exo	3	insignificant decompositon
Crysoine	1 2	225 350	350 500	290 360	Exo	13 8	not a good separation of steps
Azorubine	1	175	350	?	Exo	2.6	low mass loss on a large temperature range
Amarant	1 2	150 420	220 500	220 500	Exo	30.8 22.3	steps separated by a slow and continuous mass loss

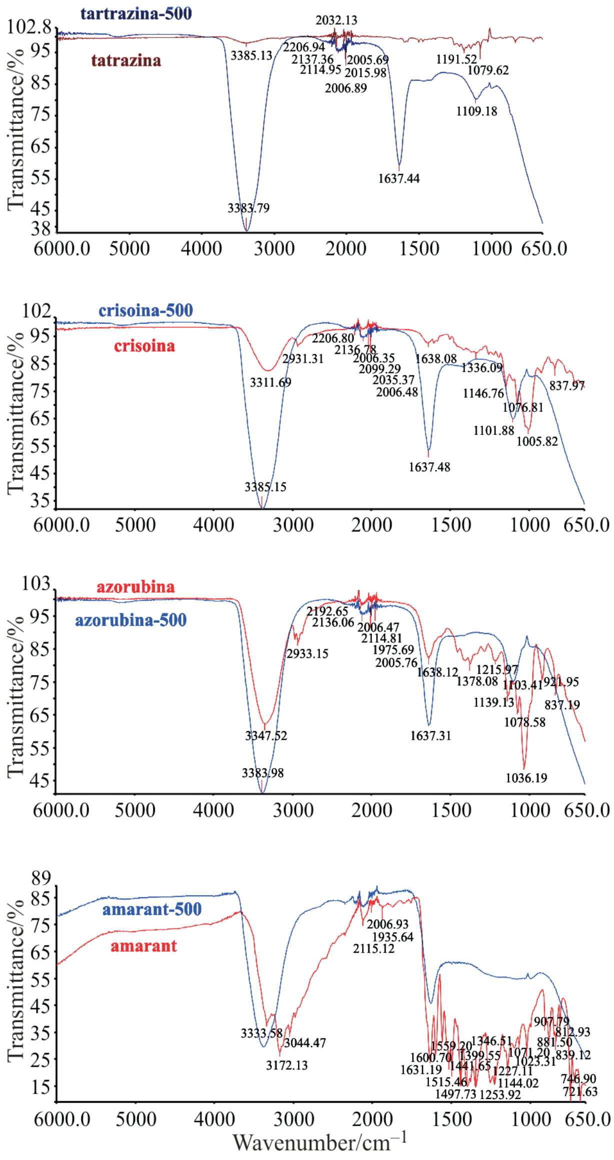

Fig. 3 Comparative FTIR spectra

Regarding the FTIR spectra of the thermally decomposed samples, the data are systematized in Table 2.

The well-developed band around 3380 cm^{-1}, present by all samples, is probably connected with the observed high hygroscopicity.

The band by 1575–1630 cm^{-1}, assigned to the diazo group, is present by all samples, before and also after the thermal treatment.

The band by 1100 cm^{-1}, assigned to ionic sulphonate, is not present by Amarant residue, and this is probably in connection with its high degradation degree (more than 50%).

Kinetic analysis

- The analysis started with the Flynn–Wall [4] and Ozawa [5] method. The TG data obtained by different heating rates β are processed according to equation:

$$\ln\beta = \ln\left[A\frac{f(\alpha)}{\mathrm{d}\alpha/\mathrm{d}T}\right]_\alpha - \frac{E}{RT} \tag{1}$$

where A – preexponential factor in the Arrhenius equation, $f(\alpha)$ – conversion function, E – activation energy, R – gas constant, β – heating rates.

The data are presented in Table 3.

According to the very sharp TG curve for tartrazine, there is also a narrow dispersion of the E values. But generally, a variation of the activation energy *vs.* conversion was observed.

In a first approximation, the main values of E can be used; these values correspond to a conversion degree of 0.4–0.5.

- For reasons of comparison, we continue the kinetic analysis with the Friedman's differential-isoconversional method [6], using the equation:

$$\ln\left(\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right) = \ln[Af(\alpha)] - \frac{E}{RT} \tag{2}$$

Table 2 Characteristics of FTIR spectra after the thermal decomposition

Compound	Present wavenumber/cm^{-1}	Assignments
Tartrazine	3384 1637 1109	3380–3385 cm^{-1} O–H stretching, free OH; hydrogen bonded OH;
Crysoine	3385 1637 1102	1575–1630 cm^{-1} N=N stretching; various azo compounds;
Azorubine	3384 1637 1103	1100–1110 cm^{-1} ionic sulphonate; SO_3^{2-} ion
Amarant	3380 1580	

Table 3 Activation energy by applying FWO method

Compound	E/kJ mol^{-1} for conversion α									
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	main
Tartrazine	128.6	127.9	127.4	126.9	126.5	126.1	125.8	124.6	123.3	126.3
Crysoine	104.8	135.0	160.8	182.5	202.4	243.0	247.5	226.8	190.5	188.1
Amarant	63.1	66.4	68.7	73.9	80.8	87.7	92.3	100.7	115.6	82.3

Table 4 Activation energy *vs.* conversion by Friedman's method

Compound	E/kJ mol^{-1} for conversion α								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
Tartrazine	23.2	24.7	20.7	28.6	33.2	39.9	60.4	76.8	14.9
Crysoine	123.3	168.3	209.0	235.3	252.7	303.9	263.1	213.9	199.0
Amarant	75.8	74.0	88.8	154.4	214.9	219.4	245.1	247.3	217.7

Table 5 Kinetic parameters by NPK method

Compound	λ/%	E/kJ mol^{-1}	A/min^{-1}	m (Eq. (7))	n (Eq. (7))	$\Sigma E\lambda$
Tartrazine	99.4	133.5	$1.278\cdot10^{10}$	1	3/2	132.7
Crysoine	50.5	198.6	$11.094\cdot10^{18}$	3/2	1	183.2
	46.5	178.3	$3.022\cdot10^{16}$	0	1/2	
Amarant	87.0	82.3	$3.795\cdot10^{9}$	3	0	75.9
	11.2	38.4	$1.763\cdot10^{4}$	1	1	

The data are systematized in Table 4.

Again a significant variation of E *vs.* α was observed, and, unfortunately, this variation is not monotonous, so that data processing strategies based on a certain function $E=f(\alpha)$ cannot be used. Also the corresponding data by Friedman's method are quite different from that by FWO method and the range of dispersion are larger in comparison with the data in Table 3.

- The kinetic analysis continues with the non-parametric kinetics (NPK) method by Nomen and Sempere [7–9]. In applying this method by difficult cases we are encouraged by the results in our previous papers [10–12].

By this method it is accepted that the reaction rate can be expressed as a product of two separable functions:

$$r_{ij} = f(T_j)g(\alpha_i) \tag{3}$$

Consequently, the experimental points obtained by different heating rates β, can be expressed in a 3D space, with the coordinates of (T_j, α_i, r_{ij}).

These points are interpolated by a proper algorithm and a continuous surface of the reaction rate (according to Eq. (3)) is obtained.

Also as a consequence of Eq. (3), this surface can be suitable discretizated into an $i\times j$ square matrix:

$$M = \{r_{ij}\} \tag{4}$$

The columns account for the temperature T_j and the rows refer to conversion degree α_i, so that the Eq. (4) can be rewritten as:

$$M = \{g(\alpha_i)f(T_j)\} \tag{5}$$

The NPK method uses the singular value decomposition (SVD) algorithm [13] to decompose the matrix M:

$$\mathrm{M} = \mathrm{U}\,(\mathrm{diag}\ \mathrm{s})\mathrm{V}^{\mathrm{T}} \tag{6}$$

In this way the influence of the conversion respective temperature are separated since:

- a vector u_1 given by the first column of the matrix U is analyzed *vs.* α to determine the conversion function $g(\alpha)$; we suggest the Šesták–Berggren equation [14]:

$$g(\alpha) = \alpha^{m}(1-\alpha)^{n} \tag{7}$$

- a vector v_1 given by the first column of the matrix V is searched for the temperature dependence $f(T)$; a classical Arrhenius equation was suggested.

Also the SVD algorithm allows separating two or more simultaneous steps of a complex process.

Indeed, if the observed reaction rate at α_i and T_j is:

$$r_{ij} = r_1(ij) + r_2(ij) = g_1(\alpha_i)f_1(T_j) + g_2(\alpha_i)f_2(T_j) \tag{8}$$

the corresponding matrix M became:

$$\mathrm{M} = \mathrm{U}_1(\mathrm{diag}\ \mathrm{s}_1)\mathrm{V}_1^{\mathrm{T}} + \mathrm{U}_2(\mathrm{diag}\ \mathrm{s}_2)\mathrm{V}_2^{\mathrm{T}} \tag{9}$$

and so two independent vectors u_1 and u_2 for simulating the conversion function, respectively two independent vectors v_1 and v_2 for temperature dependence should be obtained.

The contribution of each step to the total process is quantitatively expressed by the explained variance, λ_i, so that $\Sigma\lambda_i=100$.

The data of the NPK analysis are systematized in Table 5.

As it was expected, by tartrazine it is only one process, whereas by amarant, and very clear by crysoine there are two simultaneous steps (also Fig. 1). The individual values of *E* are without significance if there is not compared with the former obtained data.

Our suggestion is to consider a main value of the activation energy:

$$\overline{E}=\Sigma\lambda E \tag{10}$$

The corresponding data in Table 5 agree very well with the data of FWO method (Table 3). The advantage of applying the NPK method is a less speculative way for obtaining the kinetic parameters necessary to describe, even if formal, the reaction rate of a complex decomposition process.

Conclusions

- Knowledge on the thermal behavior of food additives is essential for processing food into a safety board. The necessity of combining the thermoanalytical data with the study on the changes in the FTIR spectra due to the decomposition process was proved.
- Tartrazine, crysoine, azorubine and amarant exhibit quite different thermal behavior, despite of a rather similar structure. From the most stable tartrazine to the less stable amarant there are great differences in the thermal behavior, not necessary in connection with the molecular architecture. By the thermal degradation there appear some OH and hydrogen bonded OH groups, probably due a destructive oxidation. Destructive changes of the sulphonate group are also observed.
- The kinetic analysis was difficult due to the complex process of degradation. Only by NPK method it was possible to obtain the formal rate equation for the separate steps.
- By considering the individual contribution of each step to the thermal process, a rather good agreement between the values of the activation energy by FWO respectively NPK methods was obtained.

Acknowledgements

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