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TG/DTG/DTA for the oxidation behavior characterization of vegetable and animal fats

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Abstract TG/DTG/DTA curves can be used to estimate alimentary fats quality and antioxidants insertion efficiency. Sunflower oil obtained from Carnia hybrid and pork lard were used as matrices for the non-isothermal measurements. The first stage of non-isothermal decomposition is mostly important for the characterization of the fats thermal stability. The corresponding onset temperature is a good value for the comparison of different fats thermal stability or for the effectiveness evaluation in case of antioxidant insertion. In this study, it can be seen a considerable improvement of the fats thermal stability by adding small amounts from a natural antioxidant liquid mixture (obtained by alcoholic maceration of equal amounts of seven plants, namely: milfoil, rosemary, marjoram, thyme, lovage, oregano, and basil). Chlorophylls removal from the plant extract using two different adsorbents was accompanied by a four time decrease of the antiradical activity (measured by the DPPH method) with Sephadex LH20 and seventeen times decrease when activated carbon was used.

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Introduction

TG/DTG curves can be used to estimate alimentary fats quality by determining the kinetic parameters and induction period of oxidation. Also, since the thermal decomposition reactions imply oxidative exothermic and endothermic processes, it is possible to estimate the energy involved by DTA and DSC techniques. Often these methods are more advantageous than the conventional ones because they are more precise and require smaller quantities of the substance and the results are obtained more quickly [1–3].

Thermo-analytic techniques are also valuable for studying the activity and stability of antioxidants used for fats protection at high temperature [4]. Several synthetic and natural antioxidants with code numbers from E300 to E321 are accepted to be used in food by the European Union, since they fulfills the European Scientific Committee for Food (SCF) safety requirements. Still there is a growing awareness of the pollution risks in biological systems and one potential cause is linked to the synthetic antioxidants [5–7]. Natural antioxidants are an interesting alternative, if the high efficiency and thermal stability of the synthetic compounds can be reached.

After a 2 years study on the antioxidant activity of several selected spice extracts from Romanian cultivars, a mixture of seven of the most active of them (basil, lovage, marjoram, milfoil, oregano, rosemary, and thyme) was selected for further "in situ" analysis [8]. Highly oleic sunflower oil obtained from Carnia hybrid and pork lard were the matrix used for antioxidants incorporation.

Materials and methods

Plant material

Herbarium information of the seven plant species which are individually numbered are as it follows: (1) basil (*Ocimum basilicum*), aerial part; (2) lovage (*Levisticum officinale*), leaves; (3) marjoram (*Maiorana hortensis*), leaves; (4) milfoil (Millefoli flos), flowers; (5) oregano (*Origanum vulgare*), aerial part; (6) rosemary (*Rosmarinus officinalis*), aerial part; and (7) thyme (*Thymus vulgaris*), aerial part. All these plants were acquired from an ecologic horticulture market, were washed with cold water and then dried at the room temperature.

Fat material

Sunflower oil from Carnia hybrid (highly oleic) and the pork lard were obtained from local producers.

Chemicals

The chemicals used were as it follows: DPPH (1,1-diphenyl-2-picrylhydrazyl) from Merck; ethanol and activated carbon from Chimopar; Sephadex LH20 Sigma-Aldrich. All chemicals and solvents used were of analytical grade.

Preparation of the extract

The dried plants were ground to a fine powder. The mixture of 10 g of powder formed from equal amounts of basil, lovage, marjoram, milfoil, oregano, rosemary, and thyme was mixed with 100 ml ethanol (analytical grade) in a dark glass vessel and left for 10 days at room temperature. The resultant extract was collected through filtration on a 0.45 μm filter paper and the tincture was kept in a refrigerator until it was needed for experiments or analysis.

Chlorophylls removal

An amount of 2 g adsorbent (activated carbon and Sephadex LH20, respectively) was stirred for 15 min with 5 g of alcoholic extract of seven plants, in order to insure the reaching of adsorption equilibrium. Sephadex LH20 was swollen in ethanol before being used. The adsorbent-extract mixtures were then filtered and the resulted solutions were analyzed by means of UV-VIS spectrometry. Their antioxidant activity was measured using the DPPH method [9].

Thermal analysis

Non-isothermal TG/DTG/DTA curves were obtained using Netzsch STA 409 Luxx device, in air atmosphere (30 mL min^{-1}) with 5 °C min^{-1} heating rate and alumina crucibles. The investigated samples were special sunflower oil—from Carnia variety—and pork lard, with and without added our special antioxidant mixture [8]. The temperature range was 20–800 °C and the sample mass of about 30 mg. The results were interpreted by the Netzch Proteus—Thermal analysis program.

Results and discussions

The seven plants alcoholic extracts proved excellent antiradical properties when tested by several methods such as the improved DPPH (1,1-diphenyl-2-pycrilhydrazyl) method [10] and the chemiluminescence method [11]. The plants tincture rendered also a remarkable antimicrobial activity against *Staphylococcus aureus*, *Streptococcus pyogenes*, *Escherichia coli*, and *Candida albicans* [8].

Some "in situ" tests for fat thermal stability were also performed by submitting samples of sunflower oil and of pork lard with and without added antioxidants to heating at 110 °C and evaluating the Peroxide Value and the specific UV absorbance at 232 and 270 nm [12] at different time intervals up to 100 h. The plant extract mixture showed comparable activity and, at some stages of oxidation, even higher than that of a synthetic antioxidant, BHT (butylated hydroxytoluene), in an amount of 75 mg/kg [8].

A step further was performed in the present research by evaluating the antioxidant activity of the plant mixture using thermal analysis.

The thermoanalytical curves TG/DTG/DTA of the Carnia sunflower oil and of the pork lard are presented in Figs. 1 and 2, respectively.

The profile of TG/DTG curves shows three stages of decomposition both for oil and for lard, as noticeable in the previous Figs. 1 and 2.

Souza, Santos and all [1] ascribed these steps to the following processes: (1) decomposition of polyunsaturated fatty acids such as linoleic acid with the formation of compounds such as dimers, trimers, and polymers; (2) decomposition of monounsaturated fatty acids such as oleic acid and (3) decomposition of saturated fatty acids, such as palmitic acid. Other authors [13] consider that all three types of fatty acids are decomposed in the first step. Anyway the onset temperature, T_{onset}, corresponding to the first stage of decomposition is the most important value for the characterization of vegetable or animal fats thermal stability, since based on the starting temperature of thermal decomposition, different types of oil stability and the effectiveness of any antioxidant supplements can be compared.

The addition of only 0.5 mL/kg fat of a plant antioxidant mixture (obtained by alcoholic maceration of equal amounts of milfoil, rosemary, marjoram, thyme, lovage,

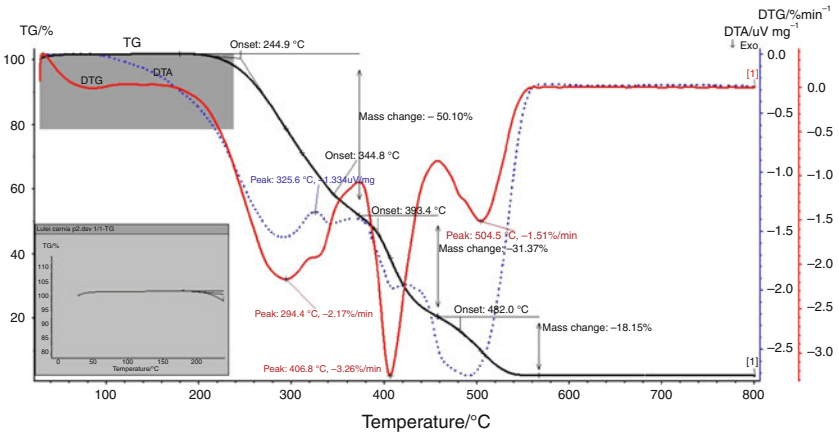

Fig. 1 TG/DTG/DTA curves for the Carnia oil

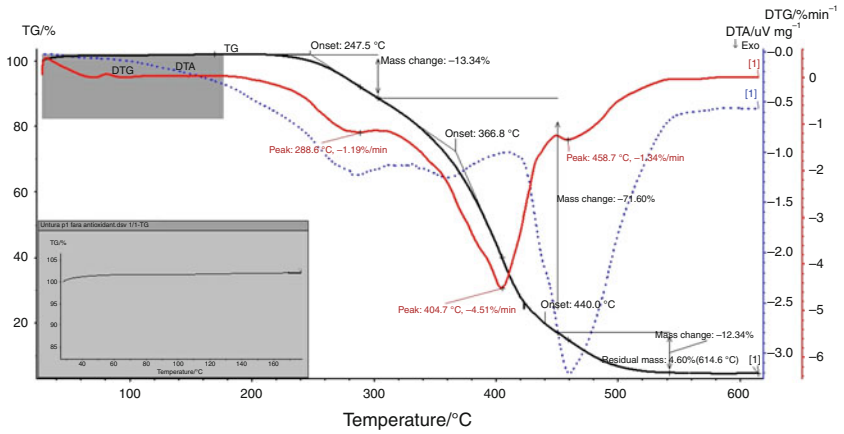

Fig. 2 TG/DTG/DTA curves for the pork lard

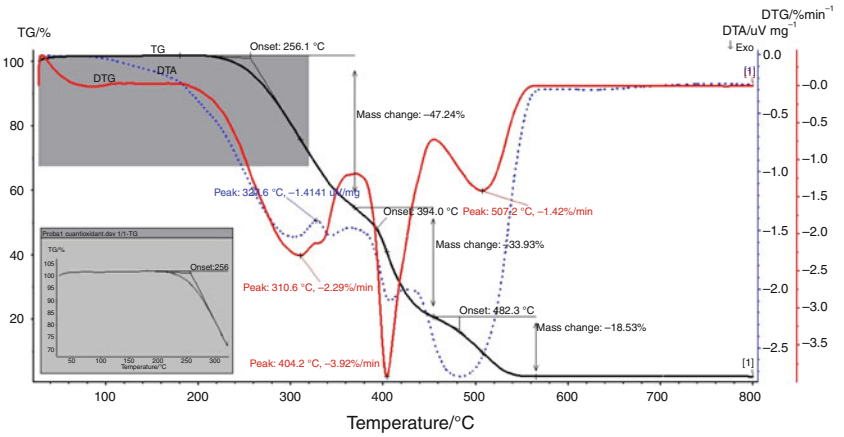

Fig. 3 TG/DTG/DTA curves for the Carnia oil with 0.5 mL antioxidant mixture/kg oil added

oregano, and dried basil) has moved the first step characteristic temperature from 244.9 to 256.1 °C (Fig. 3) in oil case and from 247.5 to 303.1 °C (Fig. 4) in lard case which shows the great efficiency of the proposed natural mixture.

DTA corresponding curves with and without antioxidants added to the fats shows three exothermic stages and an endothermic stage, located near the temperature of 325 °C. Endothermic phase probably corresponds to the polymerization of monomers formed during the decomposition of polyunsaturated fatty acids; the exothermic stages probably refers to the oxidative decomposition of saturated and unsaturated fatty acids. This assumption is reinforced by the fact that for lard, where the content of polyunsaturated fatty acids is very low, the endothermic stage has not been identified.

All tests previously described were performed in dark. When daylight is involved, the behavior of the tincture may vary due to the fact that it contains chlorophylls, porphyrin-

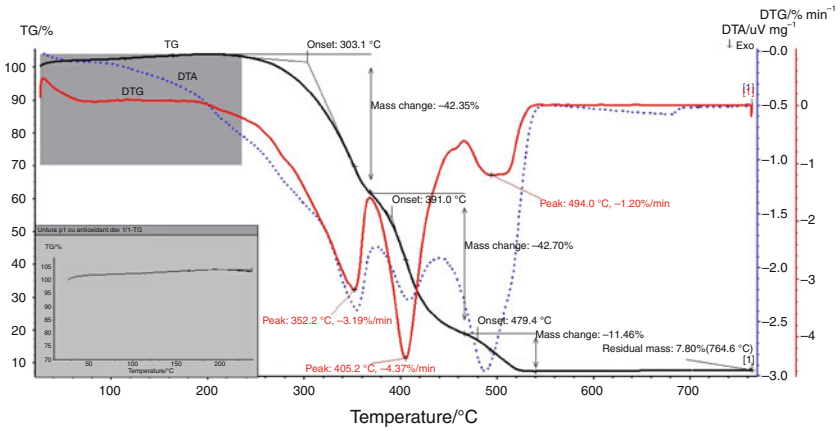

Fig. 4 TG/DTG/DTA curves for the pork lard with 0.5 mL antioxidant mixture/kg oil added

like substances which are known to be photo-sensitizers [14]. Since the presence of the chlorophylls is unwished, its removal by using solid adsorbents was performed. The activated carbon and a special resin, Sephadex LH20, were chosen for this purpose. Although some studies suggest the possibility to use Activated Alumina [15], others show this giving unsatisfactorily results [16].

In order to measure the UV-VIS spectra, the filtered solutions were diluted 100 times for the range of 220–500 nm (Fig. 5a) and 12.5 times for the range of 500–750 nm (Fig. 5b).

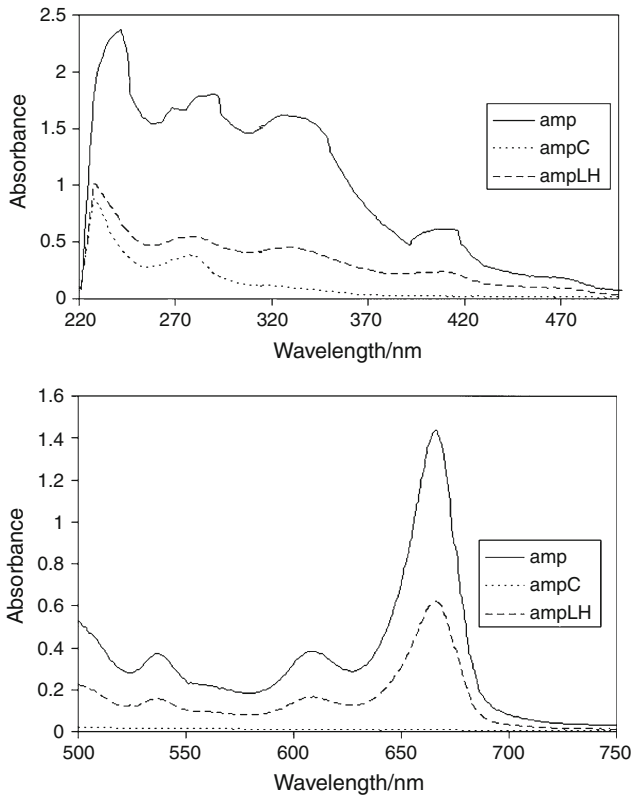

Fig. 5 **a**, **b** UV-VIS spectra of the mixture, before (amp) and after treatment with activated carbon (ampC) and Sephadex LH20 (ampLH)

From Fig. 5, it can be noticed that the chlorophylls characteristic peak intensities (541, 615, and 670 nm) decrease, when Sephadex LH20 was used. With an equal amount of activated carbon one may notice their complete disappearance. Still, when activated carbon is used, a very small number of peaks remains, which indicates a non-selective adsorption.

Due to the fact the analyzed adsorbents retains not only chlorophylls, a decrease of the overall antiradical activity is expected. This hypothesis was tested by means of the DPPH method.

The variation of the specific DPPH absorbance (517 nm) in the first 10 min after adding 0.1 ml mixture is shown in Fig. 6.

From the half-time of the DPPH, the antiradical activity (expressed as the quivalent BHT concentration) was calculated using the method described previously [10]. The results are given in Table 1.

A four time decrease of the antiradical activity was noticed in the case of the mixture treated with Sephadex LH20 and of 17 times when activated carbon was used.

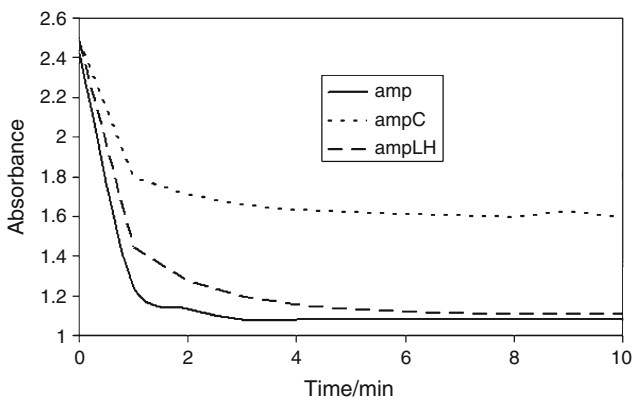

Fig. 6 The decrease of the DPPH characteristic absorbance before (amp) and after the treatment of the mixture with activated carbon (ampC) and Sephadex LH20 (ampLH)

Table 1 The antiradical activity of the mixture before and after treatment with activated carbon (ampC) and Sephadex LH20 (ampLH)

Treatment	Half-time/s	Antiradical activity/mol/L
None	3.7	0.68
Activated carbon	132	0.04
Sephadex LH20	21.3	0.17

Conclusions

The thermo-analytical methods to quantify the antioxidant/antiradical activity give results in good agreement with other methods from the literature such as chemiluminescent, DPPH, PV, and specific absorbance measurement methods.

The herbal extract obtained from equal amounts of milfoil, rosemary, marjoram, thyme, lovage, oregano, and basil proved to have an antioxidant activity comparable to BHT, both on saturated and on unsaturated fats. In order to be used under daylight conditions, removal of the chlorophylls is required, in spite of the fact that the removal procedures led to some decrease of the antiradical activity.

References

1. de Souza AG, Santos JC, Conceição MM, Silva MCD, Prasad S. A thermoanalytic and kinetic study of sunflower oil. Braz J Chem Eng. 2004;21(2):265–73.
2. Araújo KLGV, Epaminondas PS, Silva MCD, de Lima AEA, Rosenhaim R, Maia AS, Soledade LEB, Souza AL, Santos IMG, Souza AG, Queiroz N. Influence of thermal degradation in the physicochemical properties of fish oil. J Therm Anal Calorim. 2011;106:557–61.
3. López-Beceiro J, Artiaga R, Gracia C, Tarrío-Saavedra J, Naya S, Mier JL. Comparison of olive, corn, soybean and sunflower oils by PDSC. J Therm Anal Calorim. 2011;104:169–75.
4. Giuffrida F, Destaillatsa F, Egarta MH, Huga B, Golaya P-A, Skibstedb LH, Dionisia F. Activity and thermal stability of antioxidants by differential scanning calorimetry and electron spin resonance spectroscopy. Food Chem. 2007;101(3):1108–14.
5. Ssonko UL, Wenshui X. Food phenolics, pros and cons: a review. Food Rev Int. 2005;21(4):367–88.
6. Mizutani T, Nomura H, Nakanishi K, Fujita S. Hepato-toxicity of butylated hydroxytoluene and its analogs in mice depleted of hepatic glutathione. Toxicol Appl Pharm. 1987;87:166–76.
7. Williams GM, Maeura Y, Weisburger JH. Simultaneous inhibition of liver carcinogenicity and enhancement of bladder carcinogenicity of N-2-fluorenylacetamide by butylated hydroxytoluene. Cancer Lett. 1983;19:55–60.
8. Szabo MR, Radu D, Gavrilas S, Chambre D, Iditoiu C. Antioxidant and antimicrobial properties of selected spice extracts. Int J Food Prop. 2010;13(3):535–45.
9. Szabo MR, Iditoiu C, Chambre D, Lupea AX. Improved DPPH determination for antioxidant activity spectrophotometric assay. Chem Pap. 2007;61(3):214–6.
10. Szabo MR, Iditoiu C, Chambre D. New method for the calculus of the antioxidant activity in the DPPH spectrophotometric assay. Sci Tech Bull Aurel Vlaicu Univ. 2006;11:122–5.
11. Szabo MR, Iditoiu C, Chambre D, Lupea AX. Antiradical activity of some plants used in the Romanian cuisine. Int J Food Prop. 2008;2:330–8.
12. Vieira T, Regitano-D'Arce M. Stability of oils heated by microwave: UV-spectrophotometric evaluation. Ciencia Tecnol Alime. 1998;18(4):433–7.
13. Vecchio S, Campanella L, Nuccilli A, Tomassetti M. Kinetic study of thermal breakdown of triglycerides contained in extra-virgin olive oil. J Therm Anal Calorim. 2008;91(1):51–6.
14. Balaban AT, Pogany I, Banciu M. Aplicatii ale metodelor fizice in chimia organica. Bucuresti: Ed. Stiintifica si Enciclopedica; 1983.
15. Pons WA, Kuck JC, Frampton VL. Bleaching of refined cottonseed oil with modified alumina absorbents. J Amer Oil Chem Soc. 1963;40(1):10–3.
16. Cacig S. Possibilities to use vegetable extracts as natural ingredients for drugs, cosmetics and food (in Romanian), PhD Thesis Timisoara: Ed. Politehnica; 2007.