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EFFECT OF THE EXPERIMENTAL CONDITIONS ON THE THERMOOXIDATIVE BEHAVIOUR OF VEGETABLE OILS

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The thermooxidative behaviour of sunflower and rapeseed oils has been investigated by means of a derivatograph, using both dynamic and static (isothermal) temperature programs. The aim was to find the optimum experimental conditions for studying the oxidative stability of edible oils, in order to determine their storability. A novel method has been developed for the rapid indication of stability by modelling the oxidative changes under isothermal conditions.

The autoxidative deterioration, i.e. rancidification of edible fats and oils is of growing concern in the food industry. Apart from the loss caused by oxidation, the nutritional value of the products also decreases as a result of the destruction of essential fatty acids and vitamins. Fat oxidation may form toxic as well as malodorous chemicals.

Consequently, oxidative stability is one of the most important quality control parameters for the manufacturers and users of commercial fats and oils. A number of methods have been developed for evaluating the long-range stability of fatty materials, the majority of which are based on subjecting the sample to conditions that tend to accelerate the normal oxidation process [1—3].

It is generally accepted that autoxidation of fats and oils proceeds in an exceedingly complex chain reaction. Several types of oxidized compounds are formed, primarily hydroperoxides, then peroxides, aldehydes, ketones, acids, etc. Typically of chain reactions, a relatively long induction period can usually be observed, with a negligible oxygen uptake. The length of this period is characteristic of the oxidative stability (or resistance to rancidity) of the products.

Owing to the multiplicity of the reactions occurring simultaneously during the autoxidation, there are a series of parameters by which the overall degradation process can be detected. These include peroxide formation, oxygen absorption, aldehyde and ketone formation (smell), weight gain associated with oxygen uptake, and finally the heat of reaction involved.

Although the individual reactions are affected differently by temperature, catalysts and other factors, the accelerated tests are of value as a rapid indication of oxidative stability. The most widely accepted stability test for both manufacturing control and research purposes, the "Active Oxygen Method" (AOM), is

based on the determination of primary peroxides as a function of time during forced oxidation at elevated temperature.

Recently, thermoanalytical methods have also been used for the evaluation of the oxidative changes and the tendency to further deterioration of fats and oils. As regards enthalpy changes associated with autoxidation, Cross [4] has applied differential scanning calorimetry to characterize different oils and shortenings. The exothermic enthalpy change during the rapid oxidation process which follows the induction period has been detected by a baseline shift under isothermal conditions (at 155 or 170°) and in an oxygen flow. A fairly good correlation has been found between the results obtained by standard tests and DSC data. American researchers suggest microthermogravimetric and pressure differential calorimetric methods for the estimation of oil stability, using both dynamic and static programs [5, 6].

Experimental procedures

Investigations of the oxidative stability of fats and oils by complex thermoanalytical methods have not previously been published. In our experiments the derivatograph was used to study the thermooxidative behaviour of edible oils. The aim was to develop a simple, fast method for routine evaluation of the storability, i.e. oxidative stability and oxidation state.

For this purpose, fresh and aged oils were compared. The experimental models were sunflower and rapeseed oils, the most important edible oils in Hungary. Aged samples were obtained from fresh oils either by aeration at 100° for two days, or by storing at room temperature for six months. Rancidity of samples was characterized by peroxide values determined according to the standard iodometric test [7] (Table 1).

Table 1

Sample	POV, mval oxygen/kg oil
Sunflower oil, fresh	1.0
Sunflower oil, stored at room temp.	12.0
Sunflower oil, oxidized at 100°	120.0
Rapeseed oil, fresh	2.0
Rapeseed oil, stored at room temp.	15.0
Rapeseed oil, oxidized at 100°	90.0

For the study of both oxidative and thermal changes, samples were dispersed as a thin film on a ceramic block, which was a fire-brick with a large surface (1 m^2/g, measured by argon adsorption). It has been proved that this sample holder can be heated up to 1600° without change in its specific surface. A similar

block was the reference material for DTA measurements. In a few cases Pt plates were also used. Investigations were carried out under air flow (20 l/h). Sample weight was 400–450 mg.

The thermooxidative behaviour of the samples was examined under dynamic and static (isothermal) conditions. Under isothermal conditions the accuracy of temperature regulation was increased with an additional thermocouple built into the furnace atmosphere. Temperature was kept constant to $\pm 0.5°$ [8].

Results and discussion

Figure 1 shows the thermoanalytical curves of fresh sunflower and rapeseed oils obtained under dynamic conditions at a heating rate of 5°/min. For both oils decomposition proceeded in three steps. With increasing temperature, weight gain started at 140° due to oxidation and reached its maximum rate at 160° (sunflower oil) and 165° (rapeseed oil), as the DTG curves show. This process was followed by degradation from 175° to 260°, with DTG maxima at 220° in both cases. The second step of decomposition took place between 260 and 380°,

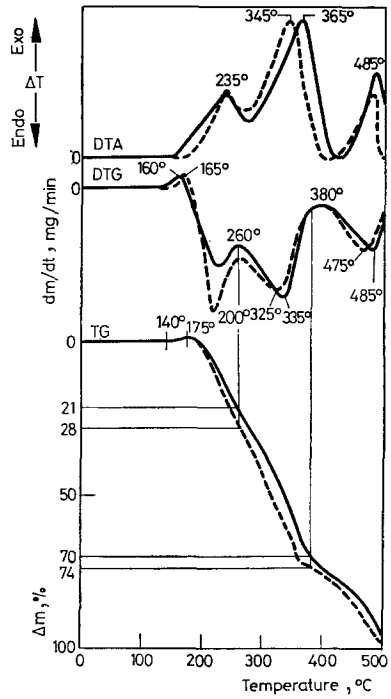

Fig. 1. Decomposition of fresh sunflower and rapeseed oils: — sunflower oil; --- rapeseed oil; heating rate: 5°/min

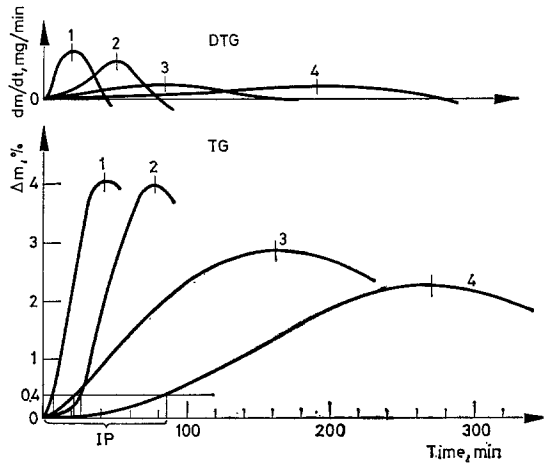

Fig. 2. TG and DTG curves of fresh (POV = 1) and aged (POV = 120) sunflower oils at 98°: 1. aged, on ceramic holder; 2. fresh, on ceramic holder; 3. aged, on Pt plates; 4. fresh on Pt plates

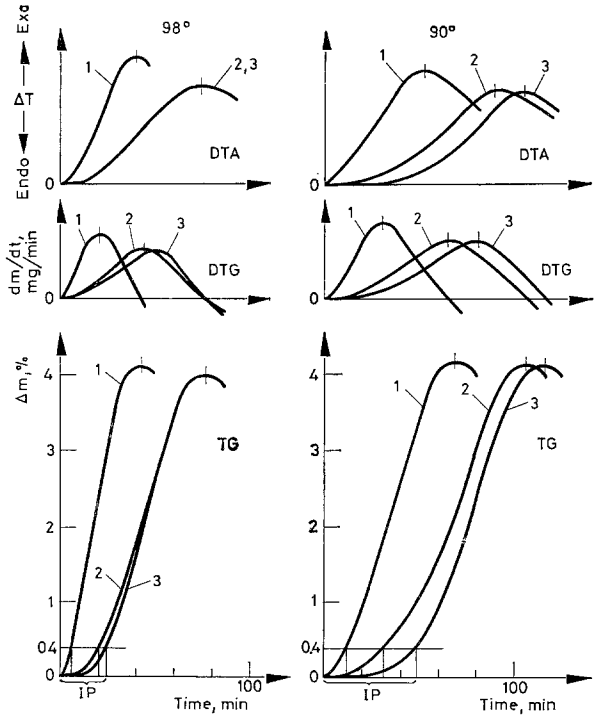

Fig. 3. Thermoanalytical curves of sunflower oils at 98° and 90°; 1. aged (POV = 120); 2. stored (POV = 12); 3. fresh (POV = 1)

and then the oils decomposed quantitatively. The DTA curves showed exothermic enthalpy changes. Since total degradation of the triglyceride molecules and combustion occurs above 260°, the first step of decomposition is decisive in the study of oxidative changes. Only slight differences could be observed between the curves for sunflower and rapeseed oils, in spite of the fact that rapeseed oil is more resistant to oxidation than sunflower oil due to its fatty acid composition.

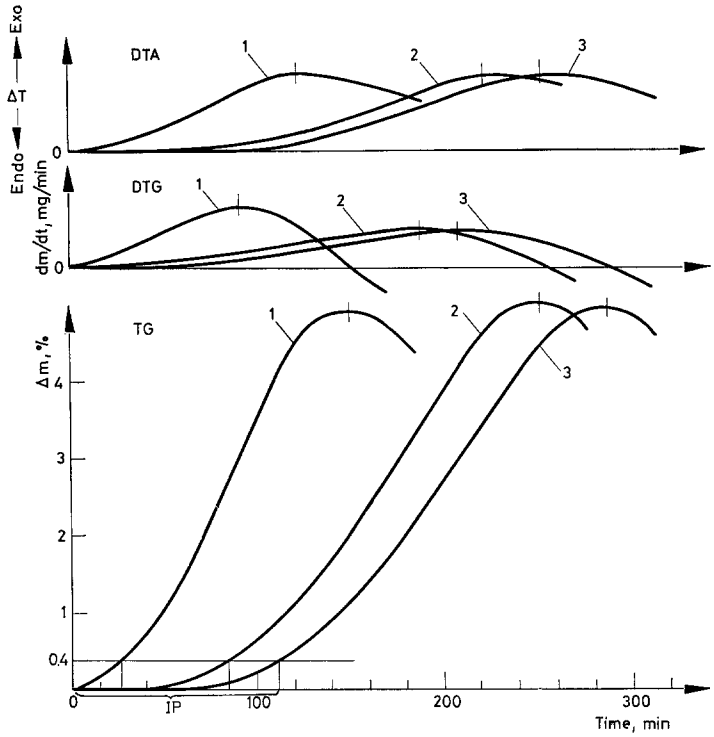

Fig. 4. Thermoanalytical curves of sunflower oils at 80°; 1. aged (POV = 120); 2. stored (POV = 12); 3. fresh (POV = 1)

To study the effect of autoxidation, we compared the degradation of fresh and aged samples. There was no significant difference between the thermoanalytical curves of fresh and oxidized oils under dynamic conditions.

Isothermal conditions proved to be suitable for evaluating storability and detecting autoxidative changes. In this case the temperature was raised rapidly (approx. 10 minutes) to the reaction temperature and TG, DTG and DTA curves were studied as a function of time.

With regard to the classical thermogravimetric method standardized by Olcott and Einset [9, 10] for the investigation of oil stability, samples were spread on platinum plates. Figure 2 presents the thermoanalytical curves of fresh and aged

sunflower oils. 98° was chosen as the reaction temperature, similarly to the standard stability test. In this case a marked difference could be observed between the thermooxidative behaviour of fresh and aged samples.

Evaluation of the TG curves was based on the classical method [9, 10]. With the technique of following the oxidation of oils by weighing samples at intervals, the length of the induction period is taken as the time elapsed from the start of the experiment to the point when the samples have gained 0.4% in weight.

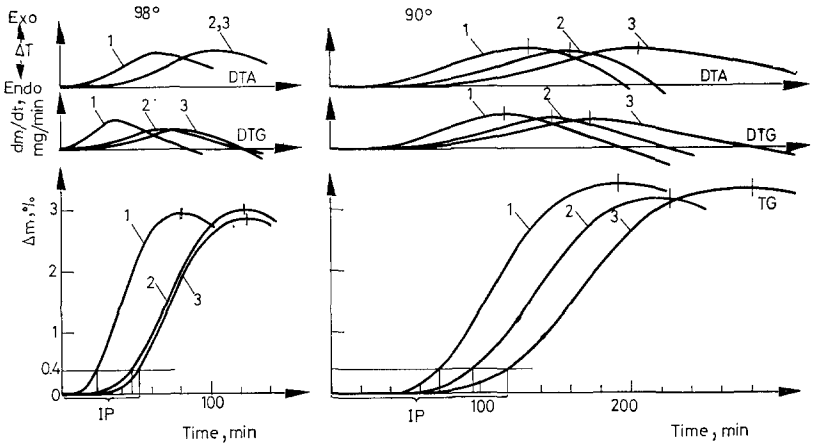

Fig. 5. Thermoanalytical curves of rapeseed oils at 98° and 90°; 1. aged (POV = 90); 2. stored (POV = 15); 3. fresh (POV = 3)

Faster reactions and larger increases in weight could be observed when the oils were dispersed on the ceramic sample holder.

The oxygen uptake of oils at 98° is too fast to permit distinction between fresh and slightly oxidized (stored) samples. In order to model autoxidation more properly and to find optimum conditions for the study of the initial phase, the temperature was lowered. At 90°, and especially at 80°, greater differences can be found in the lengths of the induction periods, the slopes of the TG curves and the times of the TG, DTG and DTA maxima. The changes still occurred within a reasonable time (Figs 3 and 4).

Thus, the oxidative stability of the oils can be characterized by the following data:

- length of the induction period (IP) (min)
- time of maximum weight gain (TG_{max}) (min)
- time of maximum rate of weight increase (DTG_{max}) (min)
- time of maximum enthalpy change (DTA_{max}) (min)

The total weight gained (Δm) depends in practice on the experimental conditions.

Fresh, stored and aged rapeseed oils were investigated in the same way (Fig. 5). Rapeseed oil is more resistant to oxidation due to its fatty acid composition, and therefore its oxygen uptake was slower than that of sunflower oil. At 80° no measurable weight increase could be determined within 3–3.5 hours, in contrast to sunflower oil.

In practice, the determination of small differences is generally required. Consequently, sunflower oils can feasibly be studied at 80°, while 90° was found to be suitable for the evaluation of the oxidation state (storability) of rapeseed oils.

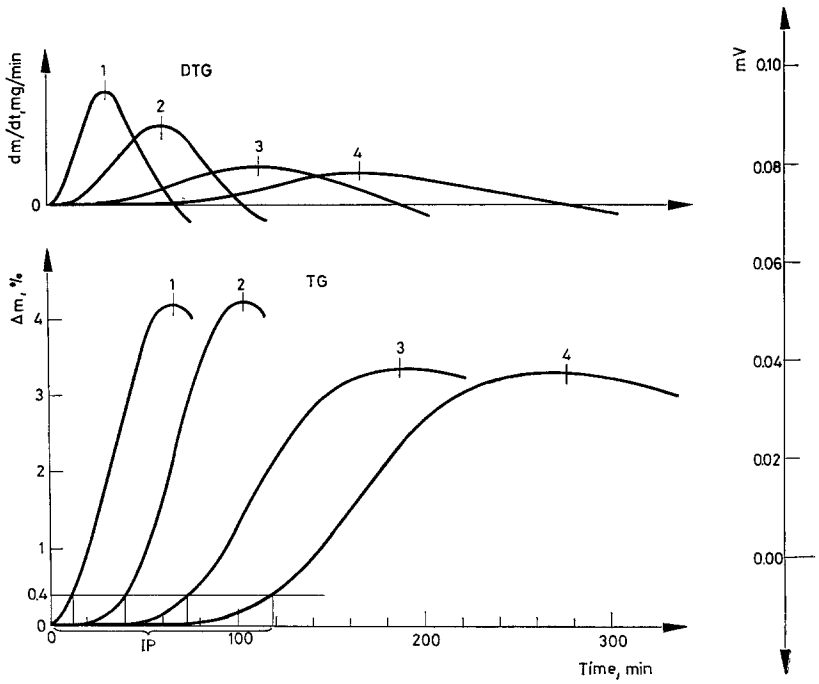

Fig. 6. TG and DTG curves of sunflower and rapeseed oils at 90°; 1. aged sunflower oil (POV = 120); 2. fresh sunflower oil (POV = 1); 3. aged rapeseed oil (POV = 90); 4. fresh rapeseed oil (POV = 2)

The thermooxidative behaviour of the two kinds of oils can readily be compared at 90°, as shown in Fig. 6. A difference between the two kinds of oils can be observed: aged rapeseed oil of high POV underwent oxidation considerably more slowly than fresh sunflower oil. This was shown not only by the lengths of the induction periods, but also by the slopes of the TG curves and by the time required to reach the highest oxidation rate, i.e. the DTG maxima. It can also be seen that under the same experimental conditions the maximum weight increase depends only on the type of the oil.

The good reproducibility of the measurements was ensured by the high accuracy of weighing. The standard deviations of the data were the following:

Data	Standard deviation. %
Induction period	±4.4
Time of DTG_{max}	±5.3
DTA_{max}	±3.4
TG_{max}	±3.4

To summarize it may be concluded that the thermal and oxidative stability of edible oils can be evaluated by means of the derivatograph. Study of the thermal decomposition under dynamic conditions enables the detection of thermal and oxidative degradation. Storability can be investigated under static (isothermal) conditions by modelling the oxidation processes. Oxidative changes can be followed quantitatively via TG and DTG curves, while DTA measurements show exothermic enthalpy changes.

This new method is also suitable for industrial quality control, and therefore we wish to extend our investigations to the study of the correlation with standard methods.

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RÉSUMÉ — On a étudié l'oxydabilité thermique des huiles de tournesol et de colza, à l'aide d'un *Derivatigraph* et en utilisant des programmes de température dynamiques et statiques (isothermes). Le but du travail était de trouver les conditions d'expérience les mieux adaptées à l'étude de la résistance à l'oxydation des huiles alimentaires afin de déterminer les conditions de leur stockage. On a mis au point une nouvelle méthode qui indique rapidement la stabilité de l'huile en reproduisant les changements d'oxydation en conditions isothermes.

ZUSAMMENFASSUNG — Das thermooxidative Verhalten von Sonnenblumen- und Rapsöl wurde mittels eines Derivatographen unter Einsatz dynamischer und statischer (isothermer) Temperaturprogramme untersucht. Der Zweck der Arbeit war die optimalen Versuchsbedingungen zur Bestimmung der Oxidationsstabilität von Speiseölen zu finden um ihre Lagerfähigkeit zu bestimmen. Eine neue Methode zur schnellen Ermittlung der Stabilität wurde mittels Modellierung der oxidativen Änderungen unter isothermen Bedingungen erarbeitet.

Резюме — Термоокислительное поведение подсолнечного и рапсового масла было исследовано с помощью дериватографа, используя обе динамические и статические (изотермические) температурные программы. Целью исследований было найти оптимум экспериментальных условий для изучения устойчивости к окислению пищевых масел, с тем, чтобы определить их срок хранения. Был разработан новейший метод для быстрого определения их стабильности с помощью моделирования окислительных изменений при изотермических условиях.