

An apparatus for the determination of induction periods of fat and oil oxidation

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Summary. A home-made version of the apparatus for the determination of induction periods of fat and oil oxidation has been described. Great attention has been paid to the choice of experimental conditions that combine good reproducibility of measurements and reasonable consumption of time. The standard deviation of the induction period determination never exceeds 0.1 h and the coefficient of variability reaches 10 % only in the case of extremely labile samples. Examples of the apparatus employment have been demonstrated on the studies of the effects of interesterification and antioxidants on oil stability.

Introduction

Fats and oils are essential parts of human food. In order to preserve and improve their quality in the continuously increasing production, a method for the determination of their oxidation stability is needed. Several of these methods exist, a great effort has been devoted in recent years to the automated version of the Swift stability test (active oxygen method, AOM) [1, 2]. It has been shown in the quoted papers that the induction period of oxidation is the most reliable quantity characterizing the oxidation stability of fats. Mechanism of the oxidation has been described by Loury [3]. Volatile products of the reaction are capable to increase the conductivity of water. Hadorn and Zürcher [2] made use of this fact and proposed the conductometric indication of the AOM endpoint.

In our laboratory we study the influence of fats and oils processing on their oxidation stability. Accordingly, our aim has been to construct an apparatus

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for the determination of the induction periods and to find such experimental conditions that combine good reproducibility and reasonable consumption of time.

Experimental method

The principle of AOM test is very simple. Air is continuously bubbled through a thermostatted sample of oil or fat. Volatile products of oxidation are carried to the conductometric cell, where they are absorbed in distilled water the conductivity of which is followed.

The detailed scheme of the apparatus is shown in Fig. 1. The air supply is provided by a diaphragm pump 1 (Rena 101, France). The air is purified by its bubbling in a washing bottle through a solution of 50 g/l potassium dichromate and 25 g/l sulphuric acid 2, then it passes through a droplets trap 3 and traces of carbon dioxide and moisture are removed over potassium hydroxide 4. The flow of air is measured by a capillary flow-meter 5 and the air enters the oxidation cell 6.

The oxidation cell is made of SIMAX glass and consists of a jacket, a test tube and a male ground joint with an inlet and outlet of the air (see detail in Fig. 1). This arrangement allows perfect cleaning of the cell, perfect heating of the sample and visible contact with the sample, as well. The diameter of the test tube is 20 mm. At the top of the tube there are two ground joints — male and female ones. The male joint joins the female joint of the jacket. The sample is at the bottom of the test tube and is heated by silicon oil that flows through the jacket from the thermostat 7. The temperature of the heating medium varies within ± 0.2 °C. The test tube is connected with the jacket and the inlet of the air at the start of the experiment.

The air containing the volatile products of oxidation exits through the outlet of the oxidation cell and bubbles through 85 ml of distilled water in the conductometric cell 8. The water is stirred with a magnetic stirrer and its temperature is kept at 9.5 ± 0.2 °C. The conductivity cell has a diameter of 45 mm and holds a conductivity electrode. The conductivity meter employed is Radelkis OK 102/1 (Hungary) 9 and the conductivity of the water is recorded with the line recorder 10 (TZ 4100, Czechoslovakia). In order to interconnect the conductivity meter and the line recorder, a simple interface has been developed.

Great attention is paid to the cleaning of the air inlet ground joint and the test tube of the oxidation cell. To avoid affecting the experimental result by metal ions [4], the glassware is cleaned by detergent and hot water using a brush.

DETAIL 6

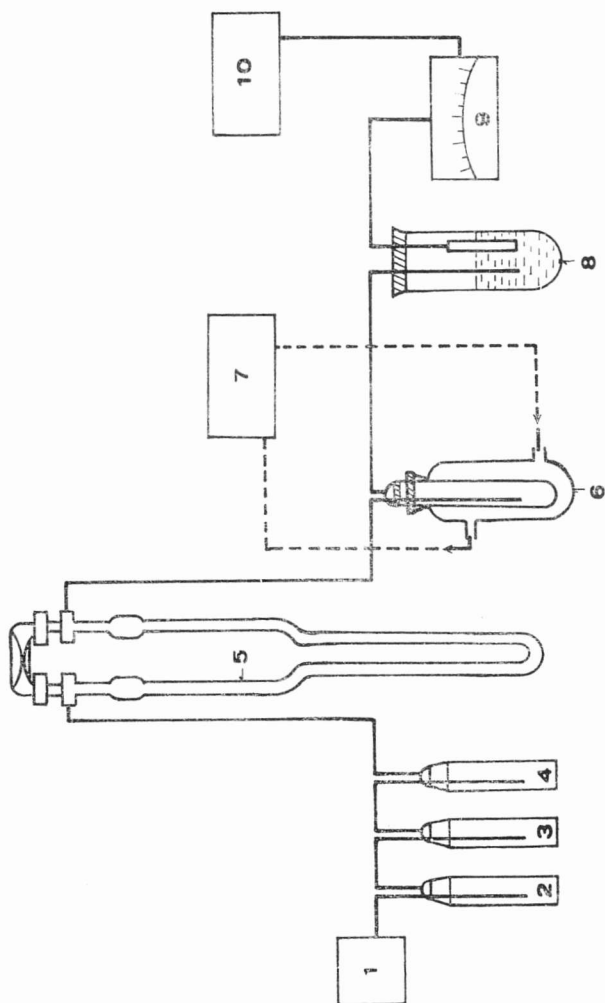
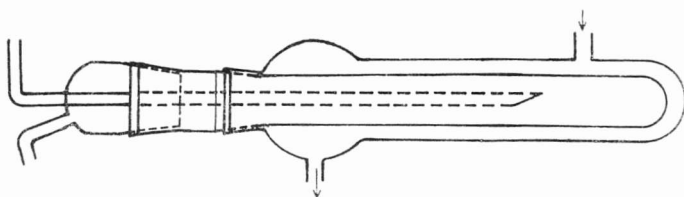


Fig. 1.: Scheme of the apparatus for the determination of induction periods. Description in text.

Then, one hour's treatment with hot ethanolic solution of potassium hydroxide follows to saponify the last traces of oils and the glassware is rinsed with hot water again and three times rinsed with distilled water. Finally, it is dried at 100 °C in an oven overnight.

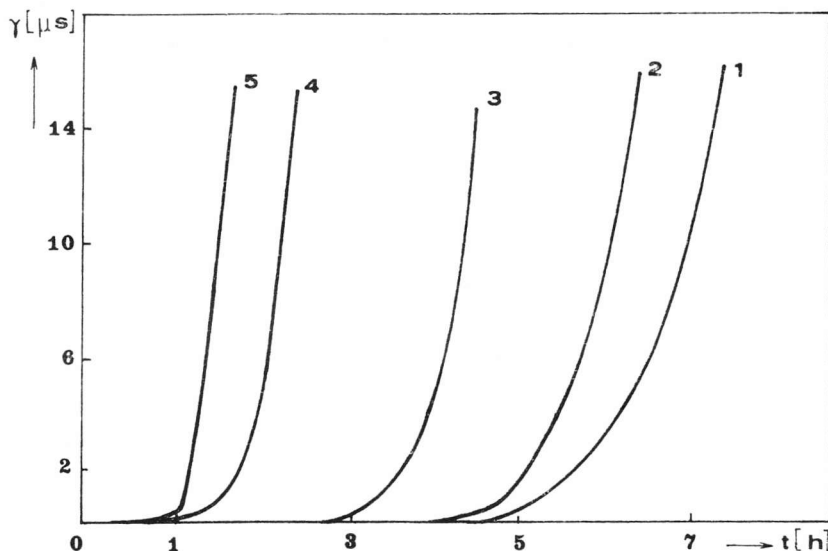


Fig. 2.: Influence of temperature on the induction periods of rape seed oil. Temperatures: 1—100 °C, 2—105 °C, 3—110 °C, 4—115 °C, 5—120 °C

The induction period (i. e., the endpoint of AOM test) is determined by extrapolation of the steeper part of the water conductivity-versus-time curve to the time axis. The intersection of these straight lines is considered as the endpoint.

Choice of experimental conditions

Temperature of oxidation

In the classical Swift stability test, the temperature of 97,8 °C is used [5], but, at this temperature, the determination of induction periods is rather time-consuming. In order to choose another temperature with lower consumption of time, we followed the temperature dependences of induction periods for several oils; a typical one is shown in Fig. 2. Comparing the results we have concluded that the temperature range between 105 and 110 °C represents the best compromise because the experiments take reasonable time (less than 1 working day) and, the distinction between oils is good (differences between

induction periods of different oils are greater than errors of the determination). We have chosen 110 °C as the temperature of oxidation.

Sample size

Hadorn and Zürcher [2] investigated the effect of sample size and have found that the curves of conductivity of the water versus time show a more distinct endpoint when a smaller volume of oil is used. Our results completely agree with their observations. The sample size we have used is 2.5 g; this is the least quantity securing perfect contact between the oil and the air.

Air flow

The effect of the air flow is shown in Fig. 3. The induction period (IP) remains the same, but, the curves become steeper and, consequently, the determination of endpoints is easier with increasing air flow. The value of 200 cm³ min⁻¹ is a limit, further increase of the air flow has no effect on the shape of curves. Therefore, we have used this flow rate in the experiments. A considerably smaller limit value, less than 40 cm³ min⁻¹, was found in [2].

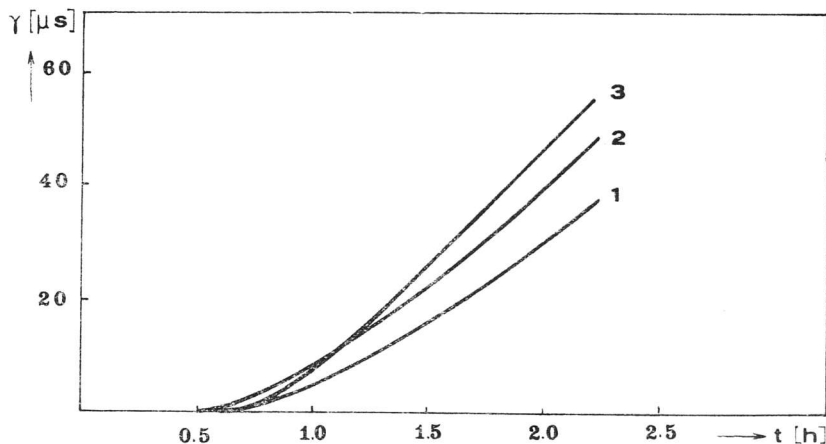


Fig. 3.: Influence of the air flow rate on the induction period determination. Flow rates: 1—100 cm³ min⁻¹, 2—150 cm³ min⁻¹, 3—200 cm³ min⁻¹.

Reproducibility

Fig. 4 shows 7 runs of AOM endpoints determination for a partly refined sunflower oil. The differences between curves seem to be great, but, the dispersion of induction periods is small. Our further results, and also the data publis-

hed in [6], resemble Fig. 4. The range of induction periods and standard deviations for five oil samples are listed in Table 1. The value of standard deviation never exceeds 0.1 h^{-1} (standard deviation is calculated as $[\sum \Delta_i^2 / (n - 1)]^{1/2}$ where Δ_i is the difference between the mean and actual values of IP and n is the

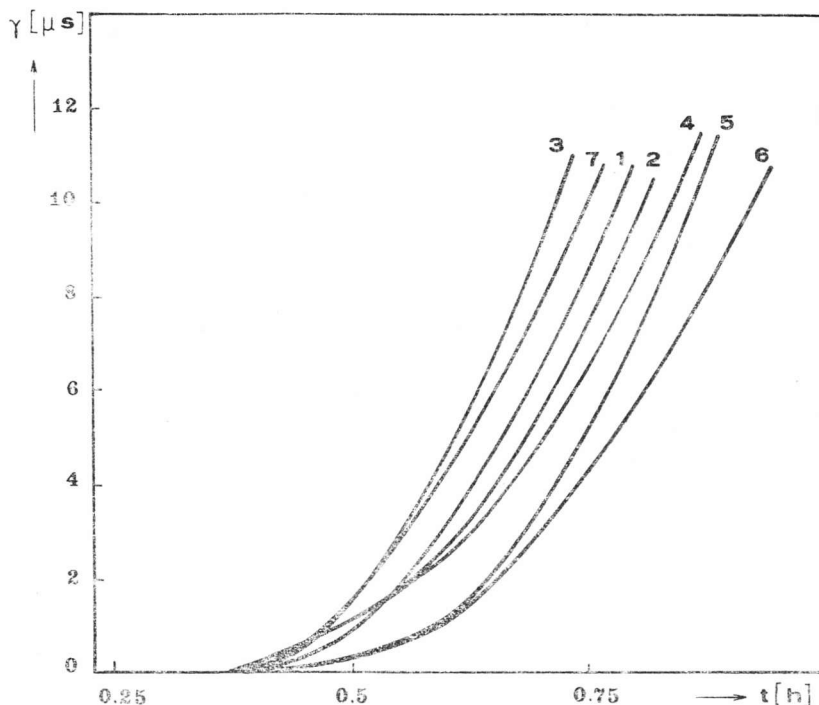


Fig. 4.: Reproducibility test of AOM determination for partly refined sunflower oil.

number of runs). Therefore, the coefficient of variability is greater for samples with a short induction period, but only in the case of extremely labile oils it reaches 10 %.

Examples of the apparatus employment

Effect of interesterification on the oxidative stability of oils

In recent years, the modification of fats and oils by the process of interesterification has been commercialized in many countries. Contradictory results have been reported in the field of the influence of interesterification on the autooxidative stability of vegetable oils [7, 8]. In our work, sodium methoxide in two concentrations was applied as the catalyst. The experimental procedure

was described previously [9]. Our results show that the mixture of lard and rapeseed oil in the mass ratio 9 : 1 was more stable — IP = 6,1 h, than the interesterified blend — IP approx. 3,5 h. Influence of the catalyst concentration — 0.2 % and 0.5 % by mass of the oil had only a negligible effect on the induction period, IP = 3,6 versus 3,4 hours. The lower stability of the interesterified blend could be due to residual soaps and methyl esters formed during randomization. Thus, subsequent chemical or physical refining and especially deodorizing process is necessary for increasing the quality characteristics of edible oils.

Tab. 1. Induction periods and standard deviations for different oil samples

Sample	Number of runs	Range/h	Mean/h	Standard deviation/h	Coefficient of variab./%
Partly refined sunflower oil	7	0,50—0,64	0,56	0,06	10,0
Sunflower oil	4	0,86—0,88	0,87	0,01	1,0
Hydrogenated sunflower oil	3	3,70—3,92	3,81	0,10	2,9
Linseed oil	3	0,85—0,96	0,91	0,08	8,8
Lard	3	0,86—0,88	0,87	0,01	1,1

Tab. 2. Induction periods (IP) of bleached rapeseed oil with added commercial sunflower lecithin

Concentration of lecithin (%)	IP/h
—	2,75
0,1	3,25
0,2	3,50
0,5	4,00
1,0	4,25

Effect of antioxidants on the oil stability

Automated AOM test is very suitable for the study of antioxidant operation in oils. Sherwin [10] reviewed the roles of oxidation and antioxidants in the various major processing steps in producing edible fats and oils. Phospholipids as antioxidant synergists in the fat autoxidation are well known, but, the mechanism by which phospholipids exert synergistic activity, is still a matter of speculation. The results presented here (Table 2) demonstrate clearly that the added commercial sunflower lecithin increased the bleached rapeseed oil stability.

Discussion

The apparatus described here enables the determination of induction periods of fats and oils oxidation. The temperature of carrying out the measurements is 110 °C. All analytical methods have their weak points and the results of accelerated tests do not always correlate with the outcome of commercial storage tests. The higher the temperature of oil samples, the greater discrepancies can occur. But, for the study of the influence of processing on the oxidation stability it is sufficient to know how a process affects this oil property. For this purpose, the use of the higher temperature is utterly satisfactory for orientation in experiments. Additionally, the very good reproducibility and small error of the measurements make possible to indicate unambiguously the improvement or deterioration of oils. Standard deviation of the measurements is generally less than of those carried out with the instrument made commercially [12], but, it can be a consequence of different temperatures of oil oxidation.

As it has been already mentioned, the construction of the oxidation cell enables a visible contact with the oil samples. This appeared to be very important, for example, in the study of the influence of phosphoric acid (common degumming agent) on the oil stability. In this case, the sample changed its colour before the endpoint had been indicated. Thus, the colour changes showed that other reactions took place in the system besides oxidation and that another, a more appropriate method of the study should be chosen.

The employment of AOM method is not limited only to the examples described above. For instance, the correlations between the degustation figure, peroxide value and induction period were investigated recently [11]. It was concluded that for most of the examined oils, the degustation figure could rather safely be predicted after a certain storage period according to IP values. Also, great usability of automated AOM method can be expected in all the fat and oil technological processes, since there is no doubt that the oxidative stability of oils can be improved by an appropriate control of refining processes.

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Аппаратура для определения индукционного периода окисления жиров и масел

Резюме

В работе описана измерительная аппаратура для определения индукционного периода, как меры оценки стойкости пищевых жиров и масел к самоокислению. Внимание уделено главным образом стандартизации экспериментальных условий, гарантирующих хорошую воспроизводимость и приемлемое время измерений индукционных периодов. Стандартное отклонение установленных индукционных периодов ни в каком случае не превышало значение 0,1 часа. Приведены примеры применения измерительного устройства для изучения влияния межмолекулярной переэтерификации TAG молекул и добавки синергентов на стойкость к окислению пищевых жиров и масел.

Aparatúra na stanovenie indukčnej periódy oxidácie tukov a olejov

Súhrn

V práci sa opisuje meracia aparatúra na stanovenie indukčnej periódy, ako miery odhadu stability jedlých tukov a olejov proti autooxidácii. Pozornosť sa venuje najmä šandardizácii experimentálnych podmienok, ktoré zaručujú dobrú reprodukovateľnosť a prijateľný čas meraní indukčných periód. Smerodajná odchýlka stanovených indukčných periód ani v jednom prípade neprekročila hodnotu 0,1 h. Uvádzajú sa príklady použitia meracieho zariadenia pri štúdiu účinku medzimolekulovej preesterifikácie TAG molekúl a prídavku synergentov na oxidačnú stabilitu jedlých tukov a olejov.