CHEMILUMINESCENCE METHOD OF RAPE OIL INVESTIGATION

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Introduction

In the last years among instrumental-analytic methods of fat examination luminescent methods are used more and more frequently.One of them is detection of chemiluminescence, i.e. spontaneous light emission in a range from 300 to 700nm, acompanying free radical fat oxidation /Loeliger and Saucy, 1984, Timms and Roupas, 1982, Usuki et al., 1979/.The oxidation substrates are unsaturated fatty acids contained main mainly in liquid fats, among others in rape oil. Rape oil in consideration of great linoleic and linolonenic acids content easily oxidized especially at higher temperature by molecular air oxygen, shows during oxidation chemiluminescence which can be detected by means of sensitive detectors of visible radiation /Mendenhall, 1977, Timms and Roupas, 1982/.Till now oil chemiluminescence investigations have been concentrated on detecting light emission of commercial vegetable oil, i.e. final refining products. It is known, however, that chemiluminescence intensity depends on such physic-l-chemical factors as temperature, light, antioxidants nd activators concentration as well as oil thermic histor; what is connected with the concentration of peroxides and peroxide radicals /Mendenhall, 1977/.

The purpose of presented paper is to investigate chemiluminescence of freshly extracted raw rape oil and attempt to apply this method for examining their accelerated oxidation.

Material

Investigation was carried out on oil extracted by petroleum benzine in Soxhlet apparatus from rape seeds on follo-

wing varieties: Jantar, Lindora, Jupiter, Jet Neuf and Górczański.The seeds of the first two varieties were obtained from the Experimental Station of Plant Breeding and Acclimatization in Małyszyn and the others from the Seed Evaluation Station in Szczecin from 1986 crops, only Górczański from 1985 crops.

Chemiluminescence detector

The measuring set applied for chemiluminescence /CL/ detection consisted of lightproof camera equipped with cooled photomultiplier EMI 9558B sensitive in a range from 300 to 800 nm, electronic amplyfing-scaling system and printing recorder /fig.1/.The 2 cm^3 sample of oil was placed in Petri dish 5 cm diameter which was then put on thermostatic stage inserted into the detection set camera.

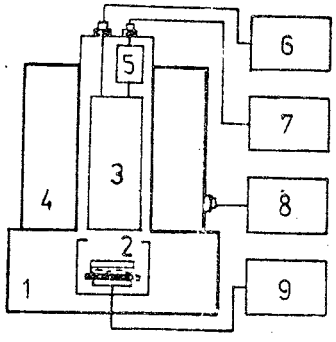

Fig.1. Block diagram of the measuring set

1-lightproof camera
2-sample on the thermostatic stage
3-photomultiplier
4-thermoelectric cooler
5-pre-amplifier
6-high tension power supply
7-electron impulse scaler with printing recorder
8-controller of the thermoelectric cooler
9-controller of the thermostatic measuring stage

Determination of chemical characteristics

Peroxide value /PV/ was measured by iodometric titration method according to PN-76/A-86918, described as Lea value. Anisidine value /AV/ was determined by Pardun procedure, except that n-heksan was the fat solvent; it expressed absorbance of oil solution with anisidine reagent at 350 nm. Totox value was formulated as 2 PV + AV /Pardun, 1976/.

Oil was exposed to accelerated oxidation in darkness in temperature 80°C in open Petri dishes 5 cm diameters. Every dish contained 3 cm^3 of oil.

All measurements were conducted in three repetitions and results were presented in the form of mean±standard deviation.

Results and discussion

Effect of temperature on rape oil chemiluminescence

The chemiluminescence intensity /I_{CL}/ dependence on rape oil temperature was determined experimentally by heating of oil on the thermostatic stage directly in the measuring camera in a range from 30°C to 90°C. The sudden increase of I_{CL} was recorded with heating. In accordance to literature that dependence is exponential, i.e. $I_{CL} \sim \exp/-E_A/kT/$, where

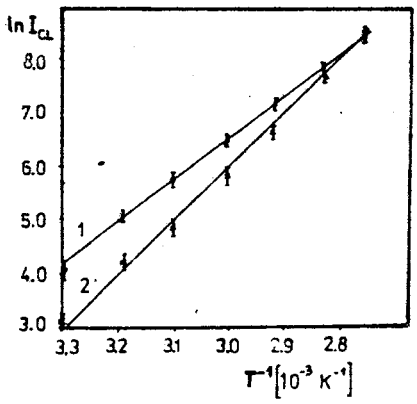

Fig.2. Arrhenius plots for rape oil extracted from seed: 1-Górczański, 2-Lindora

E_A - CL activation energy
k - Boltzmann constant
T - temperature in Kelvin

Activation energy, expressed in $kJ \cdot mol^{-1}$, can be determined as the indicator of oil capability to oxidation induced by temperature /Timms and Roupas, 1982/. Fig.2 presents relation between I_{CL} and temperature in the Arrhenius diagram for two kinds of rape oil of different activation energy. In the table 1 activation energies for examine oils calculated from diagrams are given.

Investigation of chemiluminescence kinetics in accelerated thermostatic test

The sample of rape oil was subject to accelerated oxidation in the measuring camera at 80°C, recording every 100s I_{CL} of the sample. Fig.3 shows kinetics of I_{CL} of raw rape oils during 2 hour oxidation by molecular air oxygen. Evident increase of CL intensity was observed till ca.80 min, then it reached a constant or slighty decreased. In case of rape oil from seeds of variety Górczański maximum value of I_{CL} was reached after about 6 min and then quite quick decrease was noticed. CL kinetics examination may be used for determination of fat induction period: oil of variety Górczański seeds has clearly shorter induction period then the other four oils. This method used Zelencov et al. /1978/ for milk fat.

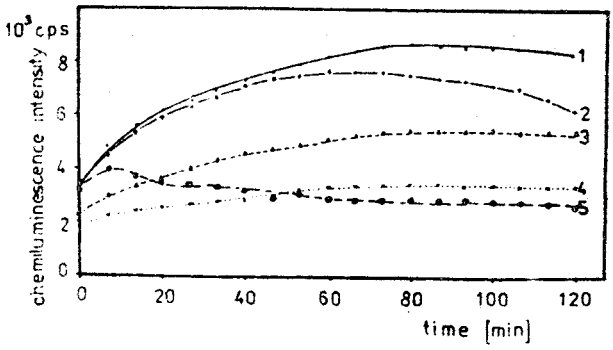

Fig.3. Kinetics of chemiluminescence during oxidation at 80°C of rape oil extracted from seeds.

Relationship between light sum and quantity of absorbed oxygen

Light sum is defined as a sum of all counts recorded at given time by the measuring system. This sum is proportional to the number of light quanta emitted by an oil sample during that time. Graphically light sum is illustrated as area under the curve $I_{CL}=f/t/$ /fig.3./. In an experiment light sum was being measured during 2 hours oil samples oxidation. As it pointed out before for different commercial vegetable oils light sum depends on the quantity of available oxygen absorbed by oil sample during oxidation /Skórska, 1987/. Oxygen concentration was calculated as subtraction of PV after and before oxidation multiplied by 16; it was expressed in ug of absorbed oxygen per one gram of oil.

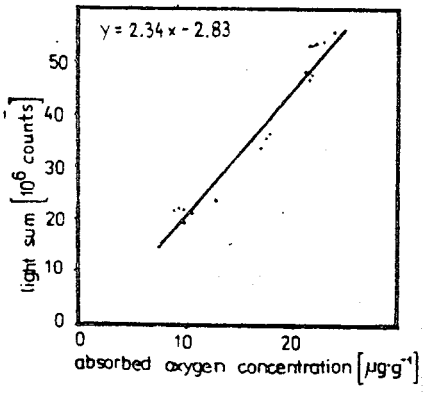

Fig.4. Dependence between light sum and absorbed oxygen concentration during oxidation at 80°C.

Also for raw rape oil the proportionality between those values was observed. Correlation coefficient was r=0.823 for n=15 and at significance level a=0.001 this relationship was highly significant.

Oil properties characteristics in the thermostatic test

The thermostatic test carried out at80°C /tab.1/ showed that there were two oil gruops of different stability.Oils from Lindora and Jantar seeds /double improved varieties/ belong to the less stable group: after 24 hours of oxidation indicate higher values of peroxide and totox unlike the three other oils.

As shown in the table, there is relationship between oil stability and chemiluminescence activation energy figured out from the Arrhenius diagram $\ln I_{CL}=f/T^{-1}$/.The higher activation energy, the less stable oil is.

Chemiluminescence parameters /light sum, activation energy/ are noticeable by small errors, thus significant differences between oil groups and varieties are evident.Although conclusions should be made carefully considering small number of investigated varieties.Probably as a result of broad investigations it will be possible to apply the quick chemiluminescence method for deterioration evaluation of oil generated from different groups of varieties.

Conclusions

1. It was found that light sum recorded during oxidation of raw rape oils is proportional to the quantity of absorbed oxygen.
2. Relationship between chemiluminescence activation energy and oxidation characteristics such as PV and totox value was noticed.
3. Chemiluminescence detection for its simpleness and no necessity to use chemical reagents can be a good method to examine rape oil oxidation.

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Table 1. Changes of rape oil characteristics during oxidation at temperature 80°C

	Górczański (N)	Jet Neuf (0)	Jupiter (0)	Jantar (00)	Lindora (00)
Peroxide value: initial	2.00±0.05	1.32±0.10	0.37±0.05	0.56±0.07	0.77±0.08
after 2 h	2.58±0.07	2.01±0.12	1.48±0.09	2.00±0.11	2.12±0.15
after 6 h	3.05±0.20	2.62±0.14	2.46±0.11	3.01±0.18	3.04±0.23
after 24 h	6.72±0.34	13.7±0.9	12.6±0.9	18.0±0.9	19.6±0.9
Absorbed oxygen concentration during 2 h ($\mu g \cdot g^{-1}$)	9.3±1.9	11.0±2.2	17.8±2.1	23.0±2.9	21.6±2.3
Light sum of chemiluminescence during 2 h (10^6 counts)	21.8±0.1	21.2±2.3	34.8±1.3	54.1±1.3	47.5±0.1
$x = \frac{\text{light sum}}{\text{absorbed oxygen}}$	2.35±0.49	1.92±0.40	1.96±0.25	2.35±0.30	2.20±0.23
Anisidine value: initial	3.62±0.54	1.87±0.35	1.94±0.45	1.36±0.23	2.63±0.24
after 6 h	6.46±0.76	2.94±0.17	2.63±0.36	3.06±0.43	4.14±0.43
after 24 h	8.21±0.24	3.80±0.18	6.28±0.41	7.74±0.27	8.44±0.47
Totox value: initial	7.62±0.64	3.87±0.55	3.85±0.55	2.79±0.37	4.17±0.40
after 6 h	12.7±1.2	8.2±0.5	7.0±0.6	10.1±0.8	11.6±0.9
after 24h	21.6±1.0	31.2±1.9	31.5±2.1	43.7±2.1	47.6±2.8
Activation energy of CL between 30°C and 90°C ($kJ \cdot mol^{-1}$)	63.5±0.8	68.5±1.0	68.0±1.2	78.6±1.0	80.8±1.8