Ph.D thesis

Development and application of new analytical method for monitoring the volatile substances of vegetable oils

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Introduction:

The oxidative status determines the organoleptic properties and the applicability of vegetable oils. Analytical method such as peroxide value, UV absorbance, p-anisidine value, which are traditionally applied to determine the oxidative status of the oil do not give precise information about the content and composition of the group of the examined oxidation products, moreover they use solvents and toxic reagents.

Measuring the volatile substances of vegetable oils like short chain alcohols, fatty acids, ketons and aldehydes, the secondary oxidation products could be characterised. A new analytical method based on headspace Solid Phase Microextraction (HS-SPME) was developed in this study to measure the volatile compounds from the headspace of vegetable oils. HS-SPME is a solvent free technique, which can be easily installed in any gas chromatographic laboratory.

In the first part of the experimental work the optimal conditions and the reliability of the method were determined. The effectiveness of the developed method was compared to different static and dynamic headspace techniques. The applicability of the method was proved by determining the volatile compounds of different edible oils. The formation and removal of volatile substances were monitored during seed crushing, crude oil storage, refining (by physical and chemical way) as well as during continuous and interrupted frying. Changes occurring in course of bleaching and deodorisation were deeply investigated.

Thesis:

- Optimising the conditions of the method it was established that the 2 cm long Carboxen / divinylbenzol / polydimethylsiloxane fiber is the most sensitive and has the best selectivity away the examined ones. 2 g of oil in a 30ml vial, 45-min extraction at 80°C, and 5-min desorption at 250°C found to be optimal to monitoring the volatile compounds of edible oils.
- Determining the amount of the extracted compounds the repeatability and reproducibility standard deviation was the same (26,4%). Examining the number of the extracted compounds, repeatability standard deviation was 10,3%, while the reproducibility standard deviation was 14,0%
- Comparing the different headspace methods HS-SPME was found to be more sensitive and less selective than static headspace analysis, while both tested dynamic techniques were more sensitive than the developed HS-SPME. method
• Searching a characteristic volatile compounds for different edible oils, it was demonstrated, that alpha-pinene in sunflower oil, benzaldehyde in groundnut oil, 2-isopropyl-5-methylhex-2-enal in corn oil and 4-methyl-2,5-dimethoxy-benzaldehyde in rapeseed oil is a specific volatile compound, which is not present in the other examined oils. No characteristic volatile compound was identified in soybean oil.

• Monitoring the amount of the volatile compounds during seed crushing it was found that oil dust and consequently the hull contains aldehydes in the highest amount. It was explained by the high surface of the dust exposed the direct contact with air. It was presented that during dehulling the amount of volatile materials decreased.

• Monitoring the changes during storage and regular refining of sunflower oil it was demonstrated that the amount of the aldehydes in deodorised oil is strongly influenced by the storage time of the crude oil. Results verified that although no important change was detected by traditional measurements, the crude oil became more unstable and sensitive for oxidation during storage.

• Analysing industrial samples, it was demonstrated that in case of both physical and chemical refining of sunflower oil, the bleaching and the deodorisation steps have the strongest effect on the amount and composition of volatile compounds.

  In a detailed examination of bleaching it was found that the activity and the dosage of the bleaching earth influence the formation of volatile materials. Applying more activated earth, the amount of volatile substances of the bleached rapeseed oil increased in higher extent than in case of a less activated earth at the same dosage. A change in the composition of the volatile materials was also observed during bleaching. In case of the more activated earth the E,Z- and the E,E-2,4-decadienal can be detected at a dosage as low as 0.6%. Using the less activated adsorbent these compounds formed in detectable amount at an earth addition of 1.2%. Good correlation can be observed between the amount of volatile materials and the p-anisidine value.

  In sunflower oil deodorization test it was found that the specific aroma component (alpha-pinene) is removed during heating the oil to the operating temperature. About 3.5 hours was necessary for the entire removal of aldehydes. The E,E-2,4-decadienal was the last identified compound removed.

• It was proven by the analysis of volatile materials, that during frying the heating and cooling stages have negative influence on the oxidative status of the oil.
Publications:


3. **F. Doleschall**: *Comparison between alternative headspace techniques applied to vegetable oils* Journal of Oil Soap and Cosmetics, 6 (2001), 217-220


5. **F. Doleschall**: Determination of volatile compounds by different headspace techniques, Journal of Oil soap and Cosmetics, 49 (2000), 136-138

Oral and poster presentations:


3. **F. Doleschall, K. Recseg, Zs. Kemény, K. Kővári**: *Characterisation of vegetable oils’ oxidative state by SPME*. Poster presentation at 23rd International Symposium on Capillary Column Chromatography, Riva del Garda Italy 2000

4. **K. Recseg, K. Kővári, Zs. Kemény, F. Doleschall, J. Denise, J. Holló**: *Application of different instrumental techniques to characterise the oxidative state of vegetable oil*. Oral presentation at 23rd World Congress and Exhibition of International Society of Fat Research (ISF), Brighton Great Britain 1999
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