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The application of Differential Scanning Calorimetry (DSC) for the quality assessment of selected edible oils

Rozprawa doktorska

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Summary

Traditional methods of assessing oil quality, including oxidative stability and authenticity, often involve time-consuming and environmentally unfriendly chemical analyses. Therefore, the aim of the study was to investigate the possibility of using the instrumental technique of differential scanning calorimetry (DSC) for the comprehensive characterization of cold-pressed edible oils, i.e. flaxseed, camelina and hempseed oil, obtained from different cultivars, in terms of assessing oxidative stability and its changes during storage as well as the possibility of assessing authenticity of oils and detecting adulteration with refined oils. In order to assess the oxidative stability of oils, the DSC oxidation test was used under isothermal (oxidation induction time, OIT) and non-isothermal conditions (oxidation onset temperature, Ton), which were additionally supported by kinetic calculations. Oxidation tests performed using different analysis conditions, i.e. at temperatures of 120, 140, 160 °C (isothermal test) and heating rates at 1, 2, 5, 10, 15 °C/min (non-isothermal test), showed different resistance to oxidation of two cold-pressed oils (flaxseed and camelina oils), due to different varieties and different fatty acid composition. For a broader characterization of the oxidation process, new parameters from the oxidation curves were determined, such as OET (oxidation completion time), oxidation rate, oxidation length (Δt) and oxidation end temperature (Tend), as well as calculations of the kinetics of the oxidation process by determining the activation energy parameters (E_a), oxidation rate constant (k) and half-time coefficient ($t_{1/2}$), which allowed for a more in-depth presentation of differences in oxidative stability due to different varieties of flaxseed oil and camelina oil. The study also allowed for the demonstration of strong negative correlations between DSC parameters and conventional chemical indicators of oxidative stability, such as the peroxide value (PV) or the TOTOX index. Significant negative linear correlations were also found between the content of α-linolenic acid and DSC parameters (OIT, Ton) for various varieties of flaxseed and camelina oils. In order to investigate the possibility of using DSC oxidation parameters (OIT, Ton) to distinguish fresh oils from stored ones, the research was extended to monitor changes during 6-month storage of three oils (flaxseed, camelina, hemp) using the DSC oxidation test (isothermal and non-isothermal), as well as chemical oxidation indicators. Significant negative linear correlations of DSC parameters were obtained for all oils with chemical indicators i.e. PV, p-anisidine value (pAV) and TOTOX. It was also found that the isothermal test (OIT) at a temperature of 120 °C allowed for the most effective monitoring of oxidative changes in oils, as for these conditions the highest correlation coefficients with

chemical indicators (PV, pAV, TOTOX) were obtained, compared to the non-isothermal test. The obtained results indicated the potential of the DSC technique for assessing the freshness and changes in oil stability during storage.

The second part of the research concerned the use of melting or crystallization phase transition profiles to assess the quality of oils. The first stage focused on examining the factors influencing the phase transition profile of oils, i.e., different scanning rates and the influence of oil storage on the phase transition curves. It has been shown that the heating rate significantly affects the shape of the curve, the number of peaks, their height and position as well as the enthalpy of the transition. The heating rate of 5 °C/min was considered the most suitable for use as a fingerprint because at this rate the profiles for different varieties of the same type of oil were most similar. Using the melting profile of flaxseed oil, the influence of storage time was also examined using the statistical process control method, i.e., X-bar and R control charts, to monitor thermodynamic changes caused by 6-month storage of the oil. As a result of these studies, 16 thermodynamic parameters were identified from the phase transition curves (peak temperature, intensity and enthalpy of transition peaks), showing an increasing or decreasing tendency during oil storage, which were considered as markers of oxidative changes in the oil. Additionally, 12 stable thermodynamic parameters were determined that can be used as markers of the authenticity of flaxseed oil.

In the next stage of the research, the possibility of using entire melting profiles in the context of untargeted analysis, using 7471 variables of the normalized heat flux, was tested to distinguish cold-pressed oils (flaxseed, camelina, hemp) from refined oils (rapeseed, soybean, sunflower) with the support of chemometric methods, mainly of the Orthogonal Partial Least Squares - Discriminant Analysis (OPLS-DA). Using this method, oils were successfully classified into six distinct classes, representing each oil type, obtaining high coefficients $R^2X(cum)= 0.971$ and $Q^2X(cum)= 0.887$, which confirmed the reliability and predictive accuracy of the model.

In the last stage of the research, the possibility of using the DSC melting profiles of flaxseed oil mixed with refined rapeseed oil in various concentrations was examined to detect adulteration by comparing various classification and regression chemometric models. Regression models, in particular the artificial neural networks (ANN) model, were the most effective in predicting the adulterant concentrations in flaxseed oil samples, already at the level of 5% refined rapeseed oil addition. Equally high accuracy coefficients for detecting the level of adulteration were obtained

for the Partial Least Squares (PLS) method. Among the analyzed classification models (LDA, MARS, SVM, and ANNs), the Linear Discriminant Analysis (LDA) method showed exceptional accuracy (99.5%) in the classification of oil samples based on the level of adulteration.

To sum up, the multi-aspect series of tests conducted allowed to demonstrate the versatility and potential of the DSC technique combined with chemometric tools for assessing the quality of cold-pressed oils, both fresh and stored. The use of this analytical technique to assess the stability and authenticity of cold-pressed oils offers more sustainable alternative to traditional chemical analyses, adapting to the changing needs of the food industry according to the principles of Green Chemistry. The conducted research presents the possibilities of using differential scanning calorimetry (DSC) as a reliable analytical instrument for the characterization and authentication of cold-pressed edible oils.

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