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Abstract

Rapid Determination of Hexane Residues in Refined Vegetable Oils Using Semiconducting Metal Oxide-Based Sensors †

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Abstract: A simple, direct method for the determination residual hexane content in refined oils was developed, which makes use of commercial Semiconducting Metal Oxides (SMOX) sensors and is proposed as an alternative to the currently used standards (ISO 9832:2002, ISO 2719:2016). The main advantages are related to the direct measurement of the headspace of oil samples. The measurements are performed at an oil sample temperature of 30 °C and by spiking the samples with hexane in the 8–132 mg·kg^{-1} range, which is in line with the requirements of current standard for the maximum residue limit set by European Union regulation. Using separate measurements performed with the help of a computer-controlled gas mixing system it is possible to determine the relationship between the concentration of hexane in oil and in the headspace.

Keywords: SMOX-based sensors; refined sunflower oil; hexane contamination; safety monitoring

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1. Introduction

The most efficient process of oil extraction and, therefore, the most widely used in the edible oil industry involves the use of technical-grade hexane-based solvents. The current European Union regulations set a solvent maximum residual limit of 1 mg·kg^{-1} [1]. The state-of-the-art measurement techniques are: (1) the flash point procedure [2], which is used extensively in practice but is semi-quantitative and has a limited sensitivity (LOD 300 ppm); (2) gas chromatography (GC) indicated in ISO 9832:2002 [3], is quantitative and sensitive down to 10 ppm residual hexane in oils. However, GC entails complex sample preparation, calibration, and the use of high-priced equipment. Accordingly, developing a solution based on chemical sensors that can work with a simple sampling procedure is an extremely promising alternative.

2. Materials and Methods

In this study, three commercially available sunflower oil samples were analyzed. Their quality was assessed by measuring the peroxide and acid values according to standards [4] and [5], respectively. The determination of residual technical hexane content of the oil was carried out according to the ISO 9832:2002 standard. The gas sensor investigation was performed using commercially available gas sensors.

3. Discussion

The development of a rapid reagentless analytical method for determining residual hexane in refined oils using SMOX-based sensors was carried out in two stages: (I) the building of calibration curves for predicting hexane in headspace based on the measurements performed in a gas mixing system (GMS) with synthetic gas mixtures, and (II) the building of calibration curves for hexane prediction in oil, which was carried out on model

oil samples in a static analysis mode with simplified sampling (sensors in contact with the headspace of the contaminated oil samples) aimed for use in out-of-the-laboratory conditions.

(I) The selection of sensors was realized by comparing the performance of the commercial gas sensors using the GMS. TGS2620, TGS2600, and FIS SB-AQ1-06 were selected for further experiments (Figure 1a).

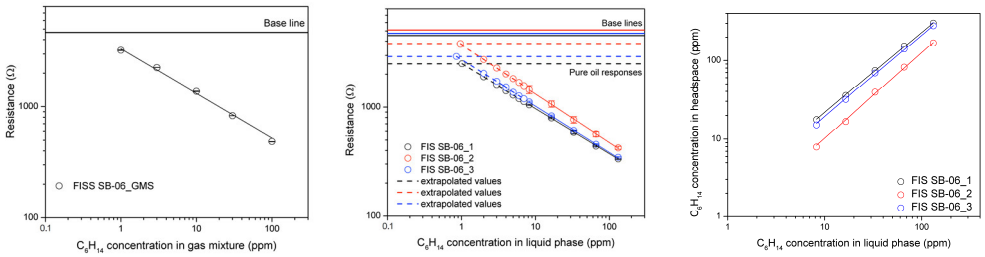

Figure 1. Calibration curves based on the DC resistance measurements for the FIS SB-AQ1-06 sensor using GMS (**a**) and the model sunflower oils from different manufacturers (**b**); the use of the transfer function obtained from GMS (**a**) to predict the equivalent hexane concentration in the headspace (**c**) of sunflower oils (**b**).

(II) The building of the calibration curves for predicting hexane in oil was based on the model samples in the following conditions: (1) the oil samples were kept at 30 °C; (2) the time allowed for the sensors to reach equilibrium when they were placed in the headspace of the oil samples was set to 30 min; (3) the hexane concentration in the oil samples, 8–132 $mg \cdot kg^{-1}$, was chosen in accordance with the application demands (Figure 1b); (4) studies of the relative matrix effect were carried out for the oil samples of various origins to take into account possible changes in their quality. One of the main research objectives was to propose a method for the prediction of the hexane content in oils using their headspace without the need for the subsequent calibration of new oil samples. Therefore, the transfer functions obtained in (I) were used to investigate the hexane distribution between the oil and its headspace (Figure 1c). The prediction of the equivalent hexane concentration in the oil headspace also allows the consideration of the matrix effect, i.e., the contribution of the interfering VOCs initially contained in the gaseous phase and reflecting the oil quality parameters (Table 1).

Table 1. Characteristics of the model sunflower oils of different manufacturers obtained using standard methods and based on the FIS SB-AQ1-06 sensor responses.

Parameters	Sample 1	Sample 2	Sample 3
Acid value, mg KOH/g	0.18	0.11	0.14
Peroxide value, meq/kg	6.1	4.1	5.0
Equivalent C(C_6H_{14}) in the headspace using GMS, ppm	2.0	0.7	1.4
Predicted C(C_6H_{14}) in the liquid phase, ppm	1.0	1.0	0.9

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References

1. Directive 2009/32/EC of the EP and of the Council on the Approximation of the Laws of the Member States on Extraction Solvents Used in the Production of Foodstuffs and Food Ingredients. Available online: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32009L0032 (accessed on 28 March 2024).
2. *ISO 2719:2016*; Determination of Flash Point—Pensky-Martens Closed Cup Method, 4th ed. ISO (International Organization for Standardization): Genève, Switzerland, 2016; 22p.
3. *ISO 9832:2002*; Animal and Vegetable Fats and Oils—Determination of Residual Technical Hexane Content, 2nd ed. ISO (International Organization for Standardization): Genève, Switzerland, 2002; 10p.
4. *ISO 3960:2017*; Animal and Vegetable Fats and Oils—Determination of Peroxide Value. Iodometric (Visual) Endpoint Determination, 5th ed. ISO (International Organization for Standardization): Genève, Switzerland, 2017; 10p.
5. *ISO 660:2020*; Animal and Vegetable Fats and Oils—Determination of Acid Value and Acidity, 4th ed. ISO (International Organization for Standardization): Genève, Switzerland, 2020; 12p.