

Potential Applications of HS-SPME/GC in Oxidized Vegetable Oils

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Abstract: Headspace solid phase microextraction chromatography (HS-SPME/GC) was evaluated as a tool in determining the rate of oxidation in oxidized soybean oil samples by measuring the production of hexanal as a secondary major volatile breakdown product of linoleic acid. Samples of the headspace taken from sealed 20 mL vials, incubated 30 min at 50 °C followed by 5 min adsorption, were injected into a gas chromatograph with 2 min thermal desorption. In applying SPME, different analytical conditions were evaluated. The linearity of response of the volatiles for the HS-SPME/GC procedure using a carboxen-polydimethylsiloxane fiber was determined from 3 g of mineral oil spiked with a hexanal standard solution at different levels. Using the optimized extraction conditions, an *R* value close to unity (*R* = 0.999) was found, and the repeatability (*n* = 11) was 6.31%. The results indicated that hexanal is linearly related to peroxide value (PV) only intermediate PV ranges (10-18 meq/kg). The study also showed that HS-SPME/GC procedure was a simple and reproducible method for the analysis of hexanal in the HS of commercial soybean oil samples, and is useful as a quality control and research tool for the evaluation of flavor quality and shelf life of vegetable oils.

Key words: Hexanal, headspace, GC, solid phase microextraction, peroxide value, oxidation, vegetable oil.

1. Introduction

Degradation of lipids results in the formation of volatile compounds that affect the flavor and safety of food products. Oxidation of unsaturated lipids results in the formation of hydroperoxides, which are tasteless and odorless [1]. Undesirable flavors and odors associated with rancidity of oxidized lipids arise from decomposition of these hydroperoxides. Lipid oxidation usually results in increases in peroxide value, hydroperoxide concentration and volatile content [2, 3].

Various techniques have been reported for gas chromatography volatile analysis in oils and oil-based foods, ranging from direct injection to various purge-trap systems [4]. Headspace gas chromatography (HS-GC) analysis is a simple technique that measures volatile compounds

equilibrated with liquid or solid samples in a closed system [5, 6]. This method has been used to analyze hexanal as a lipid peroxidation product in cereal foods [7, 8]. Capillary GC has provided a significant improvement in methodology to investigate volatile decomposition products in oxidized vegetable oils. Determination of volatile components in a mixture is a process widely used in many disciplines, such as environmental, food, forensic, oil, pharmaceutical, and polymer analysis [9-23]. Synder et al. [9] compared techniques for volatile analyses of soybean oil (SBO) including direct injection, static headspace and dynamic headspace.

A wide variety of analytical techniques for sample preparation, such as vacuum distillation, HS analysis, and supercritical fluid extraction have been developed to determine the concentration of volatile flavor components in foods.

The use of toxic organic solvents in sample preparation for volatile analysis has caused concerns

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among regulatory agencies. Ideally, sample preparation should be solvent free, simple, inexpensive, efficient, selective, and compatible with various analytical instruments [24-26]. Solvent free extractions are categorized into three areas, namely gas phase, membrane extractions, and sorbent extractions. The gas phase includes static HS, dynamic HS (e.g., purge and trap) and supercritical fluid extraction. The drawbacks to these methods include, but are not limited to, low sensitivity and cross-contamination [27].

The solid phase microextraction (SPME) technique eliminates most of these drawbacks. Sorbent extraction, however, of which solid phase extraction is the most commonly used, is simple, inexpensive, usable in the field, can be automated and uses little or no solvent. The cylindrical geometry provided by a microextraction method, called SPME, results in increased mass transfer during extraction and desorption, preventing the problem of plugging, and can readily be interfaced with analytical instruments [28].

SPME contains a fused silica fiber with an outer coating of polymeric organic liquid or solid [29, 30]. In HS analysis the coated fiber is inserted into the vapor phase above the sample. Volatilized components adsorb to the polymeric material and are extracted from the headspace. During the analysis of headspace by SPME, two equilibria should be reached by the analytes: between the matrix and the headspace and between the headspace and the coating of the fiber [27]. The theoretical aspects of HS-SPME for a three-phase system have been described in detail and generalized for a multiphase situation [28, 31].

Compare to other GC methods used for volatile analyses in foods and lipid systems, SPME is a low cost, rapid, sensitive, solventless and portable sample preparation technique. Thus, it has been applied in a variety of analytical applications since first being described by Belardi and Pawliszyn [32-49].

In the present study, HS-SPME/GC was evaluated as a tool for determining the rate of oxidation by

measuring the production of hexanal as a secondary breakdown product in oxidized SBO samples. In applying SPME different analytical conditions were evaluated. This paper describes a rapid HS-SPME/GC method to determine hexanal, a major volatile decomposition product of linoleic acid produced by SBO samples.

2. Materials and Methods

2.1 Selection of Soybean Oil Samples

Three SBO samples representing two commercial brands with different "sell by" dates and batch codes were purchased from local supermarkets.

2.2 Oxidation of Soybean Oils

Samples (100 g) of non-stripped SBO were weighed into 110 mL glass jars. Different levels of oxidation were generated in the samples by using an oven method at 60 °C, and each bottle was separately subjected to the oxidation, to establish replication. Samples for chemical and HS-SPME/GC analyses were taken every day, and peroxide value (PV) determinations using the standard peroxide value method (AOCS Method Cd 8-53) [50] were continued until PV of 20 meq/kg was reached for each treatment. A total of 17 oil samples were analyzed. For PV analysis, the oil samples were removed sequentially and were returned immediately to the same position in the oven after sampling. PV determinations were done in duplicate. The entire sampling and peroxide determination was completed in less than 30 min. After PV measurement, samples (3 g) of each oil were placed into HS sample vials, and kept in a freezer (-20 °C) until used for HS-SPME/GC analysis.

2.3 Standard

To check the linearity of calibration, a hexanal standard was obtained from the Aldrich Chemical Co. (Milwaukee, WI). Prior to use a standard for HS-SPME/GC analyses, the hexanal was purified by passing a sample of about 0.5 mL through a Waters

Sep-Pak silica cartridge (Waters Associates, Milford, MA) immediately prior to use [51], and then sealing it in a 20 mL vial under nitrogen. Accurate dilutions for the volatile standard solutions were prepared using mineral oil. A hexanal standard curve was developed using concentrations of 0.1, 1 and 10 ppm. These solutions were prepared from a stock solution (100 ppm) of standard hexanal in mineral oil which was prepared daily.

2.4 SPME Analysis

2.4.1 HS-SPME Equipment and Procedure

The SPME device consisting of a manual holder and reusable fused silica fiber assembly were obtained from Supelco Co. (Bellefonte, PA). The fused silica fiber coated with carboxen/polydimethylsiloxane (Car-PDMS) (75 μm film thickness) was studied. For HS-SPME of lipid materials, 20 mL crimp-top HS vials, with PTFE/BYTL septa, and 20 mm crimp cap aluminum seals (Agilent, USA/Germany) were used. Care was taken to clean the vials before use. For preparing a standard curve, 3 g samples of appropriate standard solutions in mineral oil were accurately weighed into tared HS vials and immediately sealed. Similarly, 3 g samples of vegetable oil were accurately weighed into tared HS vials and immediately sealed.

2.4.2 Sample Adsorption

Prior to sampling the HS, tightly closed vials containing the standards in mineral oil and SBO samples were placed and maintained in a heated (50 °C) block [26, 34] for 30 min to allow for headspace equilibration. SPME was then performed with a Car-PDMS 75 μm fiber. A sampling time from the HS of the vial of exactly 5 min was chosen. To do that the fiber assembly needle was inserted through the septum of each vial, and the fiber assembly needle was inserted through the septum of each vial, and the fiber exposed to the sample HS for 5 min. The objective was to reach equilibrium of the analytes between the fiber coating and HS.

2.4.3 SPME Desorption, Chromatography and Detection

After the HS-SPME adsorption step was completed, the fiber was then retracted into the syringe, the fiber assembly needle withdrawn from the septum, and the adsorbed substances from the SPME fiber immediately analyzed. The needle was introduced into the heated injection port of the GC to about the midpoint of the heated zone, and the injector and column oven programs initiated. Rapid and total desorption of the adsorbed substances from the SPME fiber is essential for quantification purposes. Therefore, immediately after initiation of the program, the fiber was exposed to the high temperature of the injection port in order to thermally desorb the analytes onto the column for analysis. The fiber was left in place for the required time (2 min) and the integrated peak areas obtained. The 2 min desorption time was based on literature [27] where Arthur and Pawlizyn [27] recommended sampling. Peak identification was made by using known volatile standards. Volatile compounds in SBO samples were separated, and by comparing their GC retention times with that of standard compound (hexanal), individual sample volatile peaks were identified. The GC peak areas and retention times were measured and recorded with a Hewlett Packard Model HP 6890 Integrator (Avondale, PA).

2.5 GC Conditions

A Hewlett Packard Gas Chromatograph (Model HP 6890; Avondale, PA) was used for SPME desorption, analyte separation and detection. The gas chromatograph was equipped with a flame ionization detector. The injection port was maintained at 230 °C and the detector at 250 °C. The analytes were separated with a DB-1701 column (15 m; 0.32 mm id; 1 μm film thickness; J&W Scientific, Folsom, CA). The column oven was programmed from 40 °C (2 min hold) to 80 °C at 10 °C min⁻¹ followed by a 4 min hold. Helium was used as carrier gas at flow rate 1.5

mL/min with a splitless injection mode and 2 min purge time. A short “bake-out” program was run to purge the system and removed any carryover material between runs.

3. Results and Discussion

HS-SPME/GC was evaluated as a tool for determining the rate of oxidation in oxidized SBO samples by measuring the production of hexanal as a secondary breakdown product of linoleic acid. In applying solid phase microextraction, different analytical conditions were evaluated.

The volatile compounds, generated from oxidized SBO ($n = 17$), were collected by a SPME static HS sampling method. These were analyzed by a capillary gas chromatograph with a flame ionization detector. Initial work was done to establish GC conditions and absorption/desorption times for the fiber, in order to obtain adequate resolution and maximum peak areas for the compounds of interest. Investigated GC parameters were the carrier gas flow rate (from 1.5 mL to 3 mL/min), purge time (1 min to 3 min), initial oven temperature (from 30 °C to 40 °C), and oven rate (from 5 °C min⁻¹ to 10 °C min⁻¹). HS sampling techniques were also investigated for heating time to reach equilibrium, and adsorption time (5 min) and desorption time (2 min) for the fiber.

Different analytical conditions were evaluated. Samples of the headspace were taken from 20 mL

vials incubated 30 min at 50 °C using a carboxen-polydimethylsiloxane (Car-PDMS) fiber and 5 min adsorption time. Volatiles were then desorbed into a GC using a 2 min thermal desorption. The study showed that SPME/HS-GC was a simple method for hexanal determination, and satisfactory repeatability was obtained by the method ($n = 11$, CV% = 6.31).

A manually operated SPME holder and reusable fused silica fiber (75 μ m film thickness) coated with Car-PDMS (Supelco Co., Bellefonte, PA) were used throughout the study. Page and Lacroix [52] stated that the HS-SPME efficiencies of the recently available Car-PDMS and divinylbenzene-Carboxen-PDMS (DVB-Car-PDMS) fibers were found to be much greater than those of the PDMS fibre for a number of volatile contaminants in vegetable oil lipids.

3.1 Extraction Temperature and Times

In this study, a sampling temperature of 50 °C was chosen and applied based on the literature [26, 34]. The effect of different extraction times on the analyte response from 3 g of vegetable oil using the Car-PDMS fiber was studied at 50 °C for periods from 10 min to 50 min. The sample equilibration time represents the time needed for saturation of the fiber coating. Equilibration was usually reached within 30 min (Fig. 1) and a HS-SPME temperature of 50 °C with time of 30 min was used for the remainder of the study.

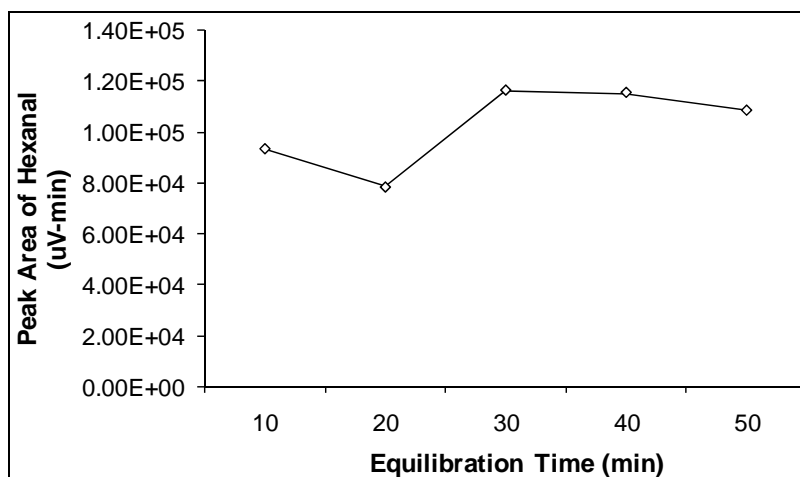


Fig. 1 Effect of sampling time on peak area of hexanal volatile fraction in mineral oil.

3.2 Studies with Oxidized Vegetable Oil

The HS-SPME/GC method was used to analyze volatiles in an attempt to draw a relationship between volatile (hexanal) profile and PV. With the experimental conditions, measurements of the oxidized SBO were made. Peak identification was made by using known volatile standard (hexanal). Hexanal was identified in the gas chromatograms of HS from oxidized SBO samples with a retention time ranging between 7.196 and 7.211 min, and the amount of hexanal was determined by GC peak area from each chromatogram. Fig. 2 represents typical chromatogram of an oxidized SBO (PV = 4.9 meq/kg). Comparison of PV data and HS-SPME/GC hexanal data from the SBO oxidation is shown in Fig. 3. The headspace hexanal content increased rapidly as PV increased from 0-5 meq/kg, but the headspace hexanal

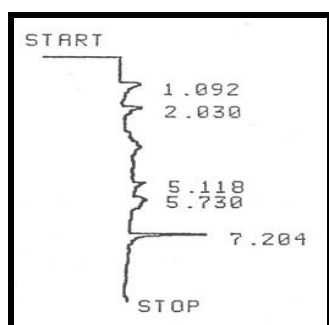


Fig. 2 GC chromatogram of volatiles from an oxidized SBO by SPME-sampled HS.

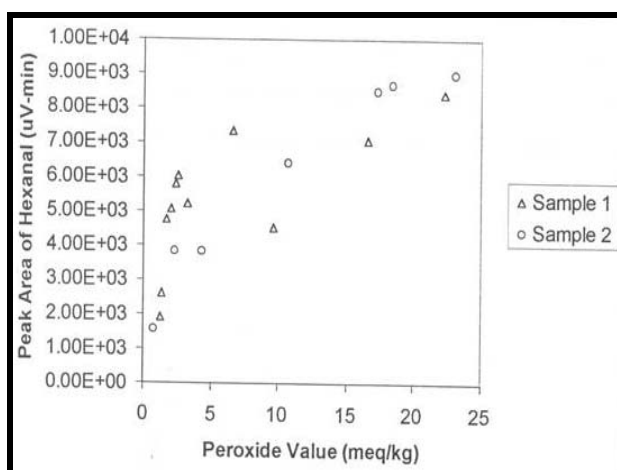


Fig. 3 Scatter plot of data for the official AOCS PV method Cd 8-53 vs. the our optimized HS-SPME/GC method for hexanal in the oxidized SBO samples.

content increased more slowly over the PV range from 5-20 meq/kg. In sample 1, one data point (PV = 10 meq/kg) appears to be an outlier, but the reason for this is not clear.

Steenson et al. [53] also used Car-PDMS, carbowax/divinylbenzene, and polyacrylate fibers, and they stated that the Car-PDMS fiber was found to have the best overall combination of sensitivity, reproducibility, and durability for analysis of compounds in the HS of SBO.

Moreover, Mateus et al. [54] preferred the similar fibre coated with 75 mL CAR/PDMS film (same thickness) in their study for the extraction, identification, and quantification of ethanol, as well. The limits of quantification were registered at levels of parts per million. Quantification of ethanol was successfully performed in fish stew and beef bib by external standard method [54].

4. Conclusions

Based on the research presented, the following conclusions were made: compared to other GC methods used for volatile analyses in foods and lipid systems, the HS-SPME/GC method is a simple, rapid and reproducible method for the analysis of volatile compounds in the headspace of commercial SBO's, and hexanal is linearly related to PV only intermediate PV ranges (10-18 meq/kg). Therefore, this method can be used as a quality control and research tool for the evaluation of flavor quality, screening for oxidation of vegetable oils.

Other advantages of the method are that it does not require special sample preparation. The solvent-free solid phase microextraction may be useful in determining the shelf life of soybean oils more rapidly and conveniently than current methods.

Further investigation should be performed to evaluate the applicability of the solid phase microextraction procedure on a variety of lipid samples, including different edible vegetable oils and their mixtures.

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