POTENTIAL APPLICATIONS OF
HS-SPME/GC IN OXIDIZED VEGETABLE OILS

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OVERVIEW

- **Background Information**
  - ✓ Problems with traditional sample preparation for volatile analysis
- **SPME**
  - ✓ Device
  - ✓ Procedure
- **Main and Specific Objectives**
  - ✓ Method development
    - ➤ Optimized extraction conditions
  - ✓ Method performance
- **Results & Concluding Remarks**

# Determination of Volatiles in a Mixture

✓ Environmental,

✓ Food,

✓ Forensic,

✓ Oil,

✓ Pharmaceutical and

✓ Polymer analyses

Problems with Traditional Sample Preparation Methods for Volatile Analysis

- Use of toxic organic solvents
  - Awareness of pollution and hazards
    - ✓ Ozone depletion
    - ✓ Carcinogenic effects
- Time consuming
- Multisteps procedures resulting in loss of analytes during the process

Eliminate or use less solvent
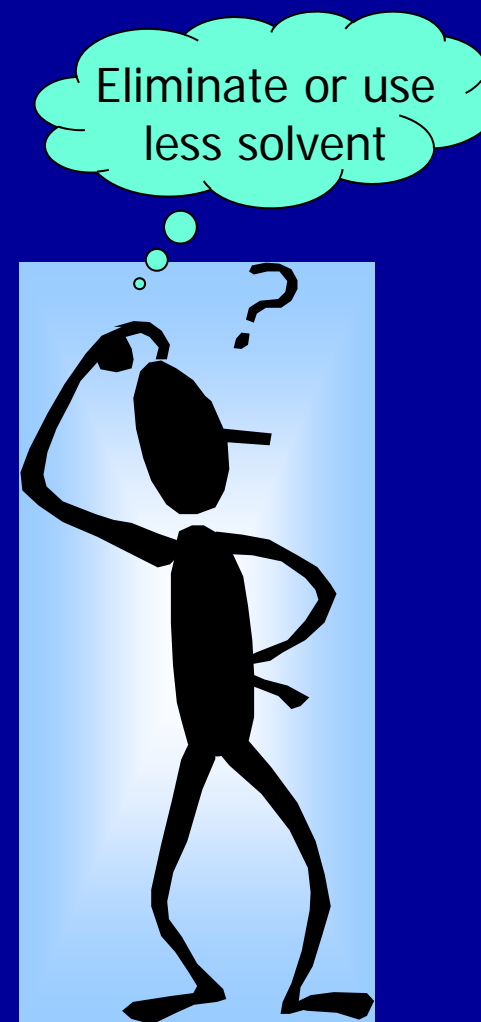
Solid Phase Micro Extraction: SPME
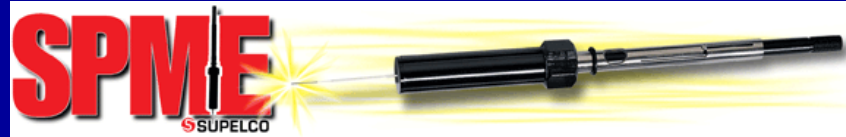

['Katı Faz Mikroekstraksiyon' *in Turkish*]

Solvent free sample preparation technique


■ Used to concentrate volatile or nonvolatile compounds

Advantages of SPME

✓ Requires no solvent

✓ Easy to automate

✓ Rapid extraction

✓ Reduce processing time

- Setup is small and convenient

✓ Simple analysis procedure

- Directly injection of fiber into GC/HPLC port

✓ Convenient for field sampling application

SPME Device

Silica core

Polymer coating

Extracting phase

Solid support
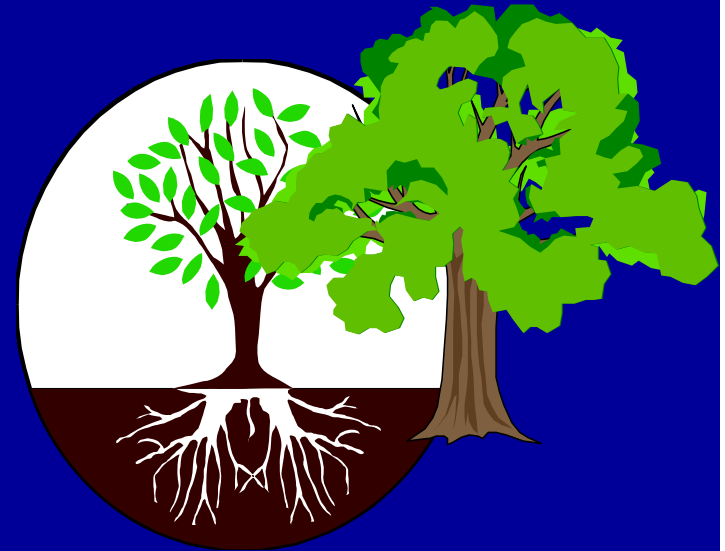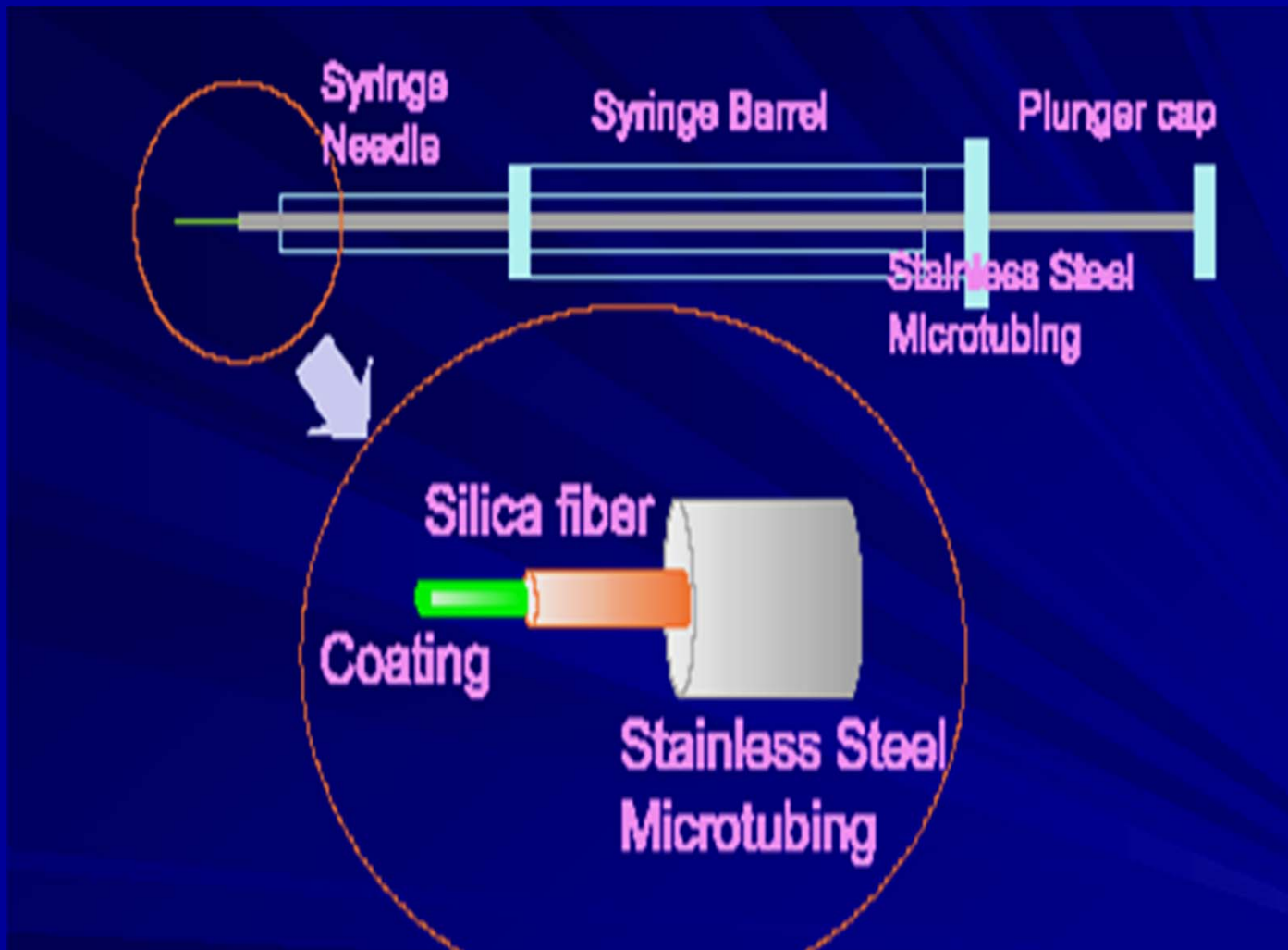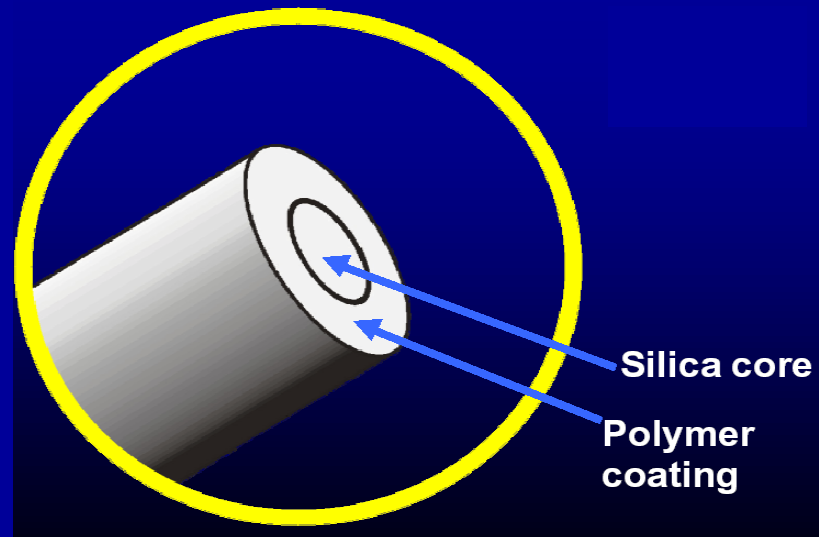
Polymer coated on outer surface of fiber

Fiber holder for automated sampling/HPLC

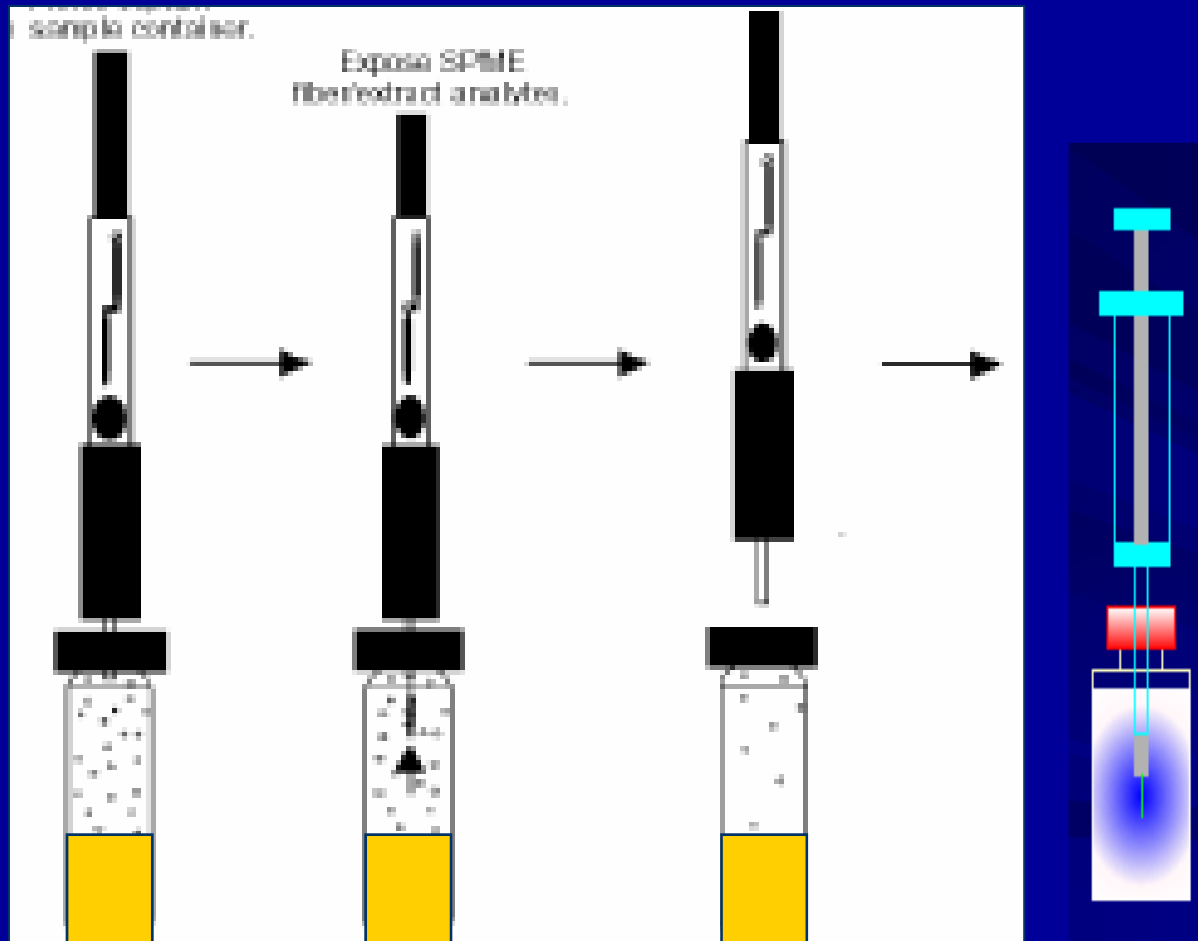Fiber holder for manuel sampling

Portable field sampler

SPME Procedure is 2 Steps

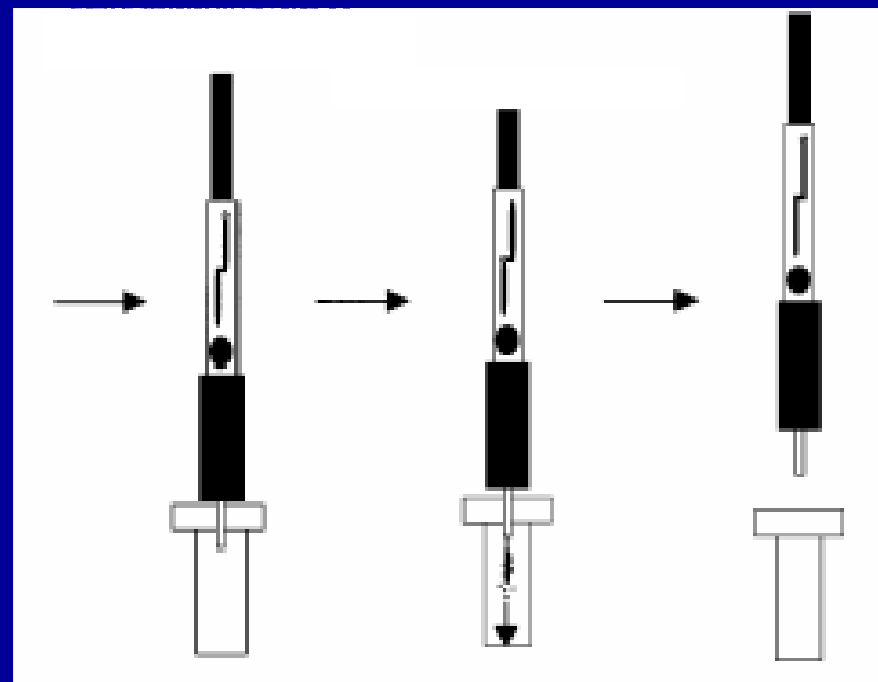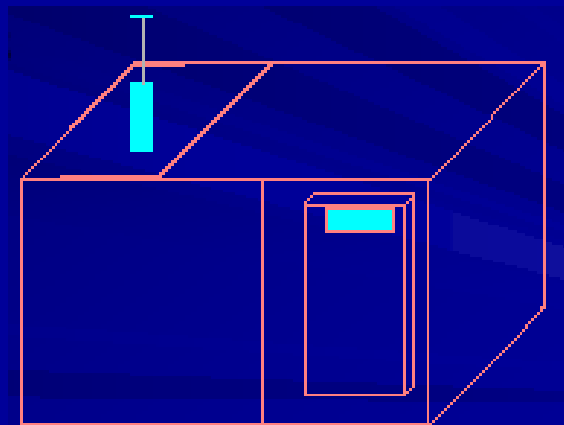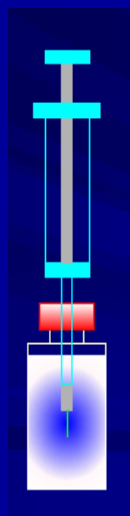## I. Step: EXTRACTION PROCEDURE

- Partitioning of analytes between the coating and the sample matrix

SPME Procedure is 2 Steps

II. Step: DESORPTION PROCEDURE

- The analytes concentrated on the coating are transferred to an instrument for desorption and analysis

The Question Will Be Answered?

Can we use this solvent free HS-SPME technique to determine the oxidation level of soybean oils?
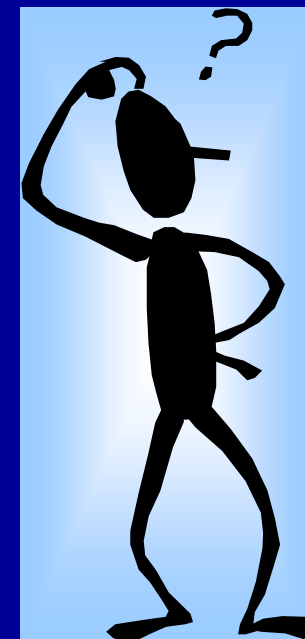
Importance of Lipid Oxidation in Food

✓ Degradation of lipids results in the formation of volatile compounds that affect the flavor and safety of food products.

✓ Lipid oxidation leads to rancidity and often it is the decisive factor determining the shelf life of food products.

✓ Oxidative rancidity also decreases the nutritional quality and safety of food by the formation of secondary products after cooking and processing.

Results of Lipid Oxidation in Vegetable Oils

- Unacceptable oil quality,
  - ✓ including loss of fat-soluble vitamins, and
  - ✓ genaration of marked off-flavors

- Lipid oxidation is also associated with
  - ✓ aging,
  - ✓ membrane damage,
  - ✓ heart disease and
  - ✓ cancer in humans.

OBJECTIVES

Main objective: To evaluate HS-SPME/GC as a tool in determining the rate of oxidation in oxidized soybean oil samples by measuring the production of hexanal as a secondary breakdown product of linoleic acid.

Specific objective: To optimize extraction conditions

Method Development

OPTIMIZATION:

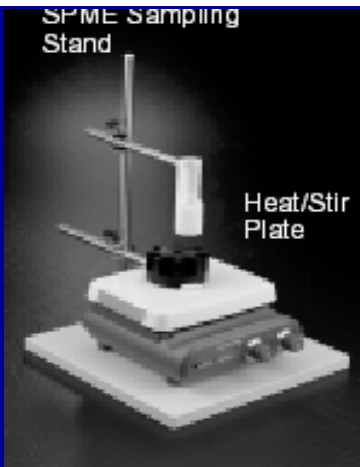Silica Fiber: Carboxen-polydimethysiloxane (Car-PDMS)

- Fiber thickness: 75 um

(Supelco Co., Bellefonte, PA)

✔ Sample volume: 3 gr in 20 ml vial

✔ Extraction time: 30 min at 50 ^{0}C

Optimization of Sampling Time
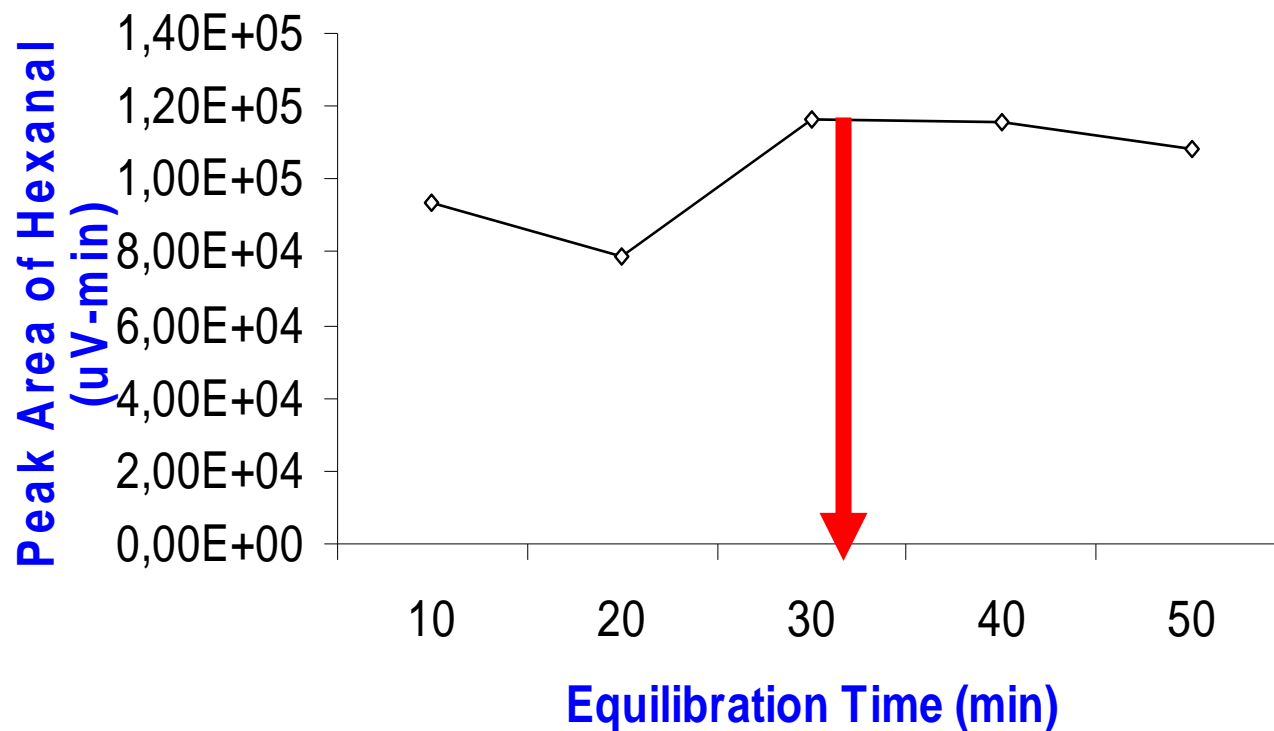
Figure 1
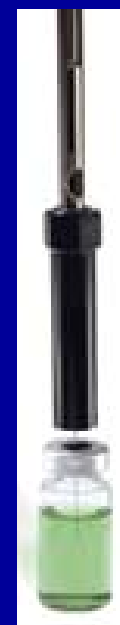
OPTIMIZATION (cont…)

✓ Sample volume: 3 g in 20 ml vial

✓ Extraction time: 30 min at 50 ^{0}C

✓ Adsorption time: 5 min

✓ Desorption time: 2 min

✓ GC conditions

GC Conditions
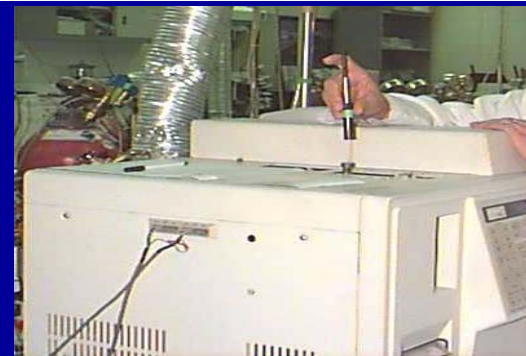
GC: Hewlett Packard (Model HP 6890; Avondale, PA)

Detector: FID

Carrier Gas: Helium

- Flow Rate: 3mL/min

Column: DB-170 (15 m; 0.32 mm. id; 1 um film thickness; J & W Scientific, Folsom, CA)

✓ Mode: splitless with 2-min purge time

✓ Injection Port Temperature: 230 ^{0}C

✓ Detector Temperature: 250 ^{0}C

✓ Oven Initial Temperature: 40 ^{0}C for 2 min

- Temperature Increasing Rate: 10 ^{0}C/min

✓ Final Temperature: 80 ^{0}C for 3 min

METHOD PERFORMANCE
Repeatability (n=11)

# OF SAMPLES	RETENTION TIME	AREA
1	7,210	69217
2	7,210	72569
3	7,208	73996
4	7,209	80541
5	7,211	74053
6	7,210	73078
7	7,209	75275
8	7,209	63433
9	7,211	71734
10	7,211	79131
11	7,211	71158

CV: 6.31%

Sampling

- Different oxidation levels of oil samples were generated using an oven method at 60 ^{0}C, and samples were stored at –20 ^{0}C in the freezer.

- PV determinations using the standard peroxide value method (AOCS Method Cd 8-53) were continued until a PV of 20 meq/kg was reached.
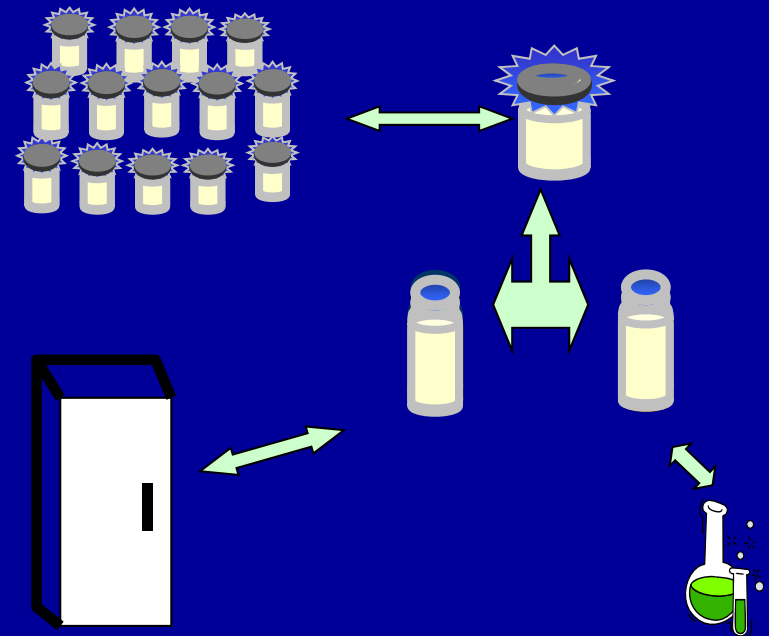
- Warner et al. (1989) reported ranges of PV for oxidized vegetable oils, to be
  - ✓ 3-5 for low oxidation,
  - ✓ 10-12 for moderate oxidation and
  - ✓ 16-18 for high oxidation

RESULTS
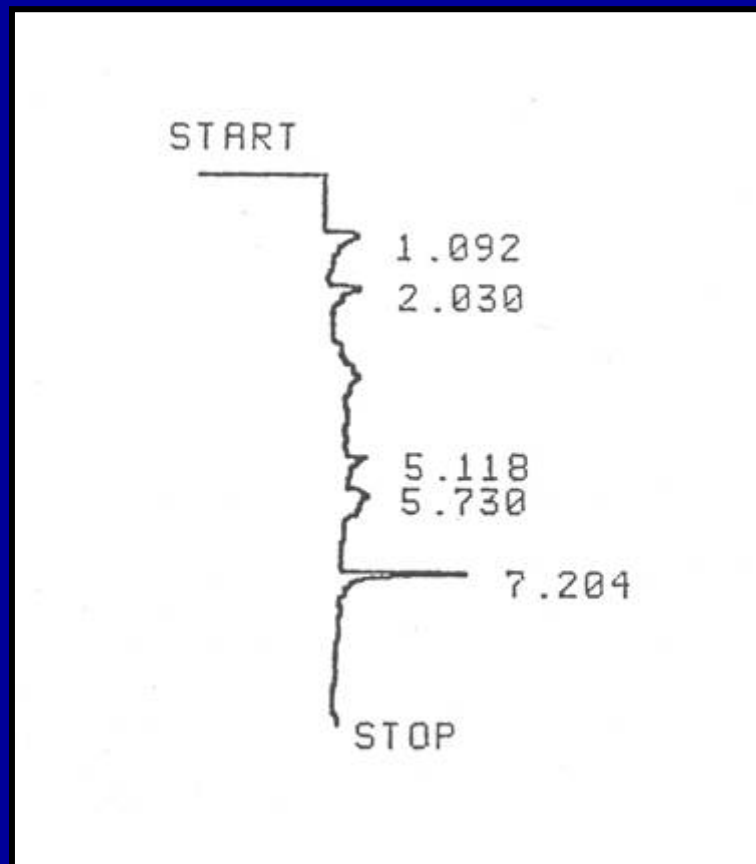
Figure 2. GC chromatogram of volatiles from an oxidized SBO by SPME-sampled headspace
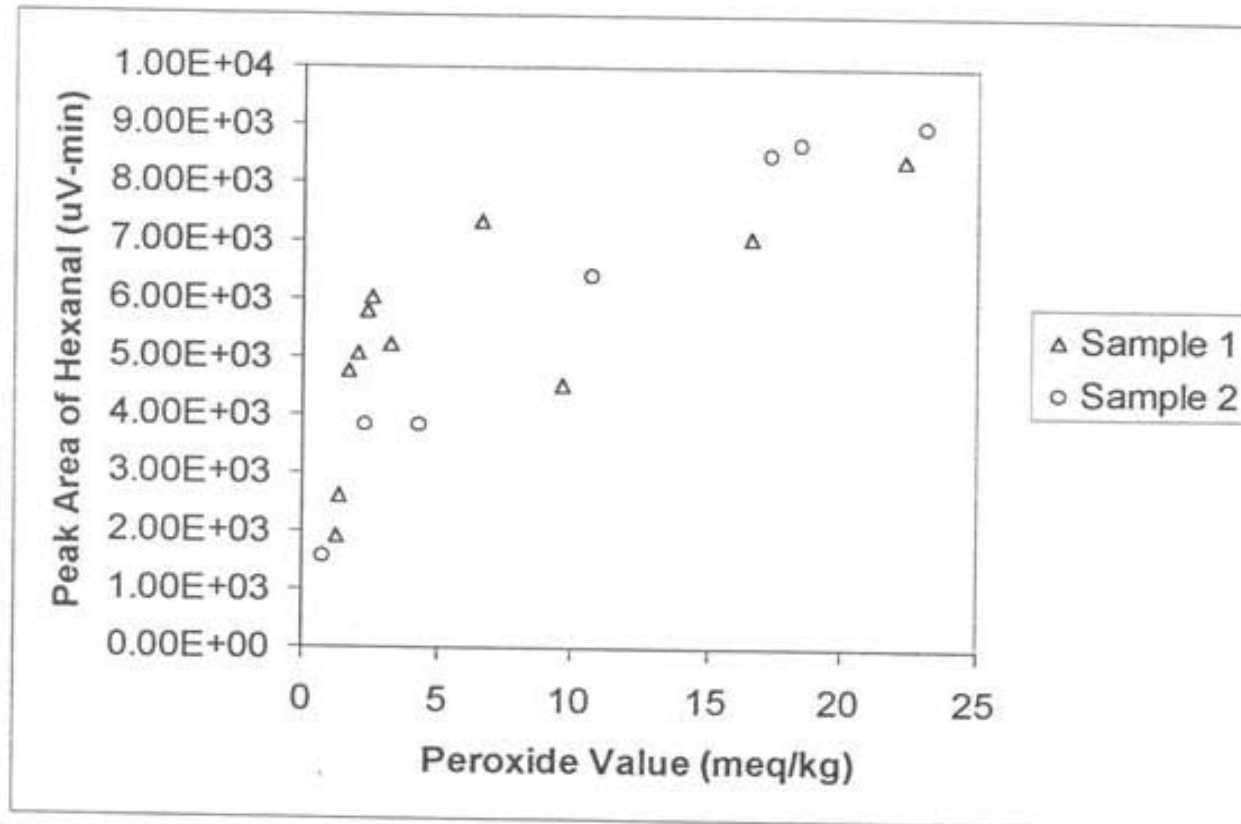
Figure 3. Scatter plot of data for the official AOCS PV method Cd 8-53 vs the our optimized HS-SPME/GC method for hexanal in the oxidized SBO samples

RESULTS…

✓   Using the optimized extraction conditions,

  ➢   an R value close to unity (R=0.999) was found &

  ➢   the repeatability was 6.31%.

✓   Hexanal is linearly related to PV only intermediate PV ranges (10-18 meq/kg).

CONCLUDING REMARKS

✓ This technique along with many other advantages that are a good alternative to traditional sample preparation methods.

✓ HS-SPME/GC procedure was

> ➤ a simple and
> ➤ reproducible method for the analysis of hexanal in SBO, and

✓ is useful as a quality control and

✓ research tool for the evaluation of

> ▪ flavor quality and
> ▪ shelf life of vegetable oil.

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NOTE: The author takes her own and full responsibility about the references cited and the use of the English language.

THANKS FOR YOUR ATTENTION…

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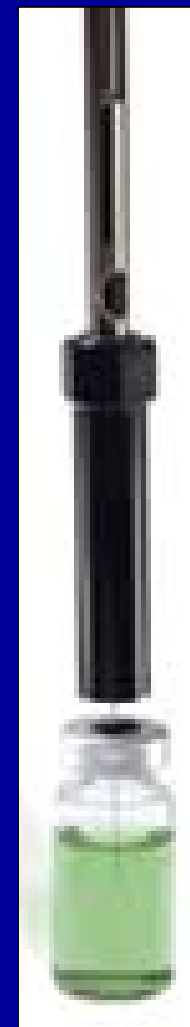http://works.bepress.com/gulgun_yildiz_tiryaki/2/

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Applications of SPME

To date, various areas

- ✓ environment (water, soil, air),
- ✓ food,
- ✓ natural products,
- ✓ medical drugs,
- ✓ biology,
- ✓ toxicology,
- ✓ testing of new products
- ✓ forensic
- ✓ polimer and
- ✓ theoretical studies

Over 400 articles were published about SPME.

SPME UNIT

❑ An injector (fiber-sparing),

❑ Silica fiber

  ▪ Fiber preserved with a protective stainless steel needle attached to a piston.

❑ Consists of fiber coating material:

  ▪ SPME fiber, liquid (polymer), solid (absorbent) or coated with a combination of both.

COLOR CODE CONNECTION

SPRING

SEPTUM SEALING

FERRULE

SEPTUM DRUM NEEDLE

FIBER SUPPORT

PHASE FIBER