# Equipment and Procedures to Measure Peanut Headspace Volatiles[1]

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**ABSTRACT**

An electronic meter was developed to measure the concentration of organic volatiles in the headspace over samples of comminuted peanuts. The meter consists of a commercially available semiconductor (Taguchi) and a temperature compensation circuit. The conductivity of the sensor increases in the presence of organic volatiles. Calibration of the meter can be made by measuring the volatiles in the headspace over known concentrations of ethyl alcohol in water. Good agreement between meter measurement of the concentration of organic volatiles in the headspace over samples of comminuted peanuts and the percent of freeze-damaged peanuts in the samples was demonstrated. Other tests with peanuts which were cured at 50 C or exposed to -1 C before curing demonstrated the meter can detect these types of objectionable flavors and indicated meter readings were not significantly affected by the moisture content of the peanuts.

Key Words: Peanuts, alcohol, aldehydes, flavor, volatiles, meter, Taguchi sensor.

Objectionable flavors in peanuts may be caused by curing peanuts at temperatures above 35 C or by subjecting peanuts to freezing temperatures before they are cured (2,7). Development of objectionable flavors in peanuts because of these treatments is accompanied by an increase in the concentration of ethanol and acetaldehyde (5). The positive correlation between the concentration of total organic volatiles and the concentration of ethanol and acetaldehyde in the headspace over comminuted peanuts (1,5,8) suggests a high headspace concentration of organic volatiles is indicative of objectionable flavors in raw peanuts. Pattee (4) developed a rapid chemical colorimetric measurement for the concentration of organic volatiles in the headspace over comminuted peanuts which employs an acidic potassium dichromate-silver nitrate reagent. Although it may be feasible to employ this colorimetric test for peanuts when they are marketed from the farm; a more simple, economical and rapid test is desirable.

A Taguchi semiconductor sensor has been used to detect combustible gases or organic solvent vapors in air (6). The Taguchi sensor is an n-type semiconductor mainly composed of tin dioxide whose conductivity increases in the presence of combustible gases or organic solvent vapors belonging to the alcohol, ketone, ester and benzol families. Watson and Tanner (9) have given a detailed description of the principle of operation of the sensor.

When comminuted raw peanut seed are sealed in a container, the partial vapor pressure of the organic volatiles in the headspace will reach equilibrium with these compounds in the comminuted peanuts. The Ostwald partition ratio to compute the concentration of alcohol in water based on its concentration in the headspace over the water solution is known, but a means to compute the concentration of volatile organic compounds in comminuted peanuts based upon the concentration of these compounds in the headspace over the peanuts is not known (3). However, the concentration of these compounds in the headspace is indicative of their concentration in the peanuts.

The objective of this study was to employ the Taguchi sensor in the development of equipment and procedures to make rapid, objective, and economical estimates of the organic volatile concentrations in the headspace over samples of comminuted raw peanuts.

## Materials and Methods

*Sensor Circuit Description.* A schematic diagram of the sensor circuit for the organic volatile meter (OVM) is shown in Fig. 1. This circuit consists of the sensor, thermister and temperature difference circuits. The TGS 812 Taguchi sensor (Figaro USA, Inc., 322 Wilshire Dr., E. Wilmette, IL 60091) is used in the sensor circuit for the OVM. The conductivity of the sensor increases as molecules of gas are absorbed. In order to achieve a faster desorption time a heater circuit is used to heat the semiconductor surface near 200 C. Seven operational amplifiers LM 324 (National Semiconductor Corporation, 2900 Semiconductor Dr., Santa Clara, CA 95051) are used between various portions of the circuit to provide isolation and amplification of output voltages.

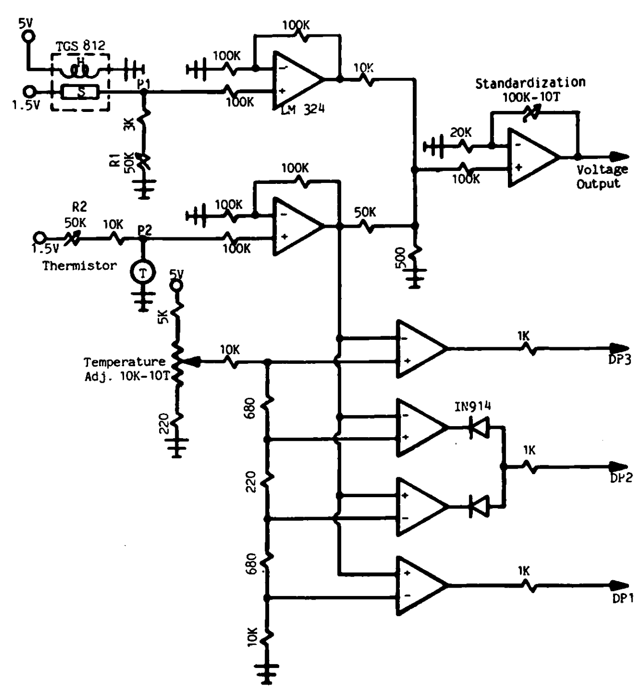


**Fig. 1 Schematic diagram of the sensor circuit for the organic volatile meter.**

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The voltage output is a sum of the sensor circuit output and the thermistor circuit output. The thermistor circuit is necessary to compensate for temperature effects on the sensor output voltage. Because the thermistor circuit provides adequate temperature compensation for only a 5 C change, a temperature difference circuit activates warning lights when the temperature changes more than ± 2.5 C after standardization of the OVM. Four operational amplifiers are used to compare the voltage inputs from the thermistor circuit to the voltage input from the temperature difference circuit. The comparators control the voltage at DP1, DP2 and DP3 (Fig. 1) at either O V or 5 V. A warning light connected to each of these three points is lighted when the voltage is O V and unlighted when the voltage is 5 V. When the voltage at the positive terminal of the comparator exceeds the voltage at the negative terminal, the output from the comparator is 5 V. When the voltage at the negative terminal is equal to or greater than the voltage at the positive terminal the output from the comparator is O V. Each time the OVM is standardized the variable resistor in the temperature difference circuit is adjusted to give a positive net voltage to all of the comparators, and 5 V at DP1, DP2 and DP3. If the temperature increases < 2.5 C the decrease in voltage output from the thermistor circuit will trigger the lower comparator in the DP2 circuit and 0 V will be at DP2. A temperature increase > 2.5 C will trigger the comparator in the DP1 circuit and O V will be at DP1 and DP2. Conversely, if the temperature decreases < 2.5 C the upper comparator in the DP2 circuit will trigger and O V will be at DP2. A temperature decrease > 2.5 C will trigger the comparator in the DP3 circuit and O V will be at DP2 and DP3.

Because all Taguchi sensors do not have the same relationship between conductivity and the amount of adsorbed gas, resistor R1 is provided to adjust the voltage at P1. The standard procedure is to place the sensor in the headspace over a solution of 1.28 mL of ethyl alcohol per L of water and adjust R1 to give a voltage of 0.75V at P1. (The procedure to prepare solutions of ethyl alcohol in water is discussed later.) Resistor R2 is provided to adjust for differences among thermisters, because the relationship between temperature and conductivity varies. The standard procedure is to control the temperature at 21 C and adjust R2 to give a voltage of 0.95 V at P2. After these adjustments R1 and R2 are not changed except when the semiconductor or thermister is changed or when the instrument is reconditioned.

*Timer Circuit Description.* To allow the Taguchi sensor to equilibrate with the organic volatiles in an atmosphere, a fixed interval of time must elapse before reading the OVM. Preliminary investigations showed good agreement among OVM readings of the same atmosphere which were taken 45 sec after exposing the sensor to the atmosphere. The timer circuit shown in Fig. 2 is used to indicate the 45 sec. delay period when OVM measurements are made.

The timer circuit includes a LM556CN dual timer (National semiconductor Corporation), resistance-capacitance (RC) circuits, a push button switch, a buzzer and two transistors. Timer A is connected to a RC circuit that triggers after 45 sec. Timer B is connected to a RC circuit that triggers after 2 sec. Momentarily closing the timer reset switch sets timer A for 45 sec and DP4 at O V. After 45 sec, DP 4 is 5 V, timer B is set, and the buzzer is activated. Two sec later the buzzer is deactivated.

*Display Circuit Description.* An Intersil 7107 LED display circuit (Intersil, Inc., 10710 N. Tanau Ave., Cupertino, CA 95014) used in the OVM is shown in Fig. 3. The voltage output shown in Fig. 1 is connected to the display input of the display circuit. The voltage at the display input is registered in millivolts on the LED display. The decimal point lights in the LED display are used for warning lights. Warning lights DP1, DP2, and DP3 (Fig. 3) are connected to the points labeled DP1, DP2, and DP3 in Fig. 1; and are lighted when the voltage is O V. Lights DP1 and DP2 come on if the temperature increases > 2.5 C or lights DP2 and DP3 come on if the temperature decreases > 2.5 C after standardization. In either case the OVM should be restandardized. Warning light DP4, connected to point DP4 in Fig. 2, is lighted when the 45 sec time-delay timer is operating.

*Meter Component Configuration.* The OVM consists of a probe connected to the meter box with a flexible electrical cable. The Taguchi sensor and the thermistor are located in the probe (Fig. 4). All of the electronic circuitry and the LED display shown in Figs. 1, 2 and 3 are contained in the meter box. Measurement of the concentration of organic volatiles within a sealed container may be accomplished by inserting the probe through a 2.9 cm diameter opening. The opening may be sealed with a No. 7 rubber stopper which is removed just before inserting the probe. When the probe is fully inserted, the flange formed by the ceramic magnet seals the opening. If the opening is through a magnetic material, the flange holds the probe in place.

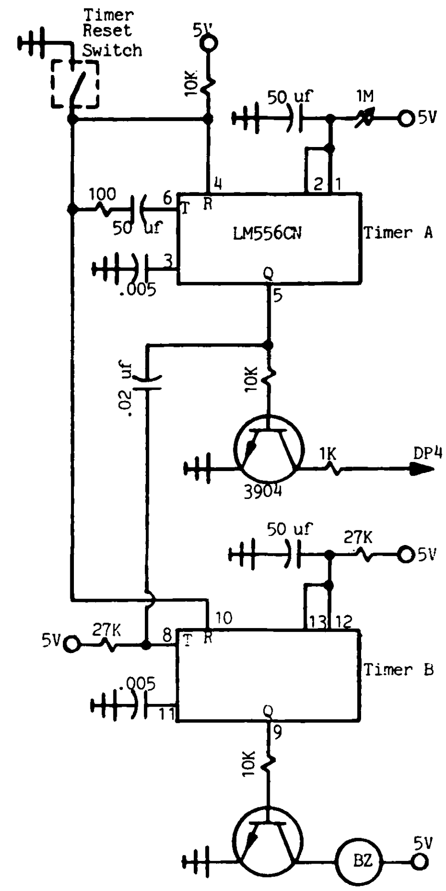


**Fig. 2. Timer circuit for the organic volatile meter.**

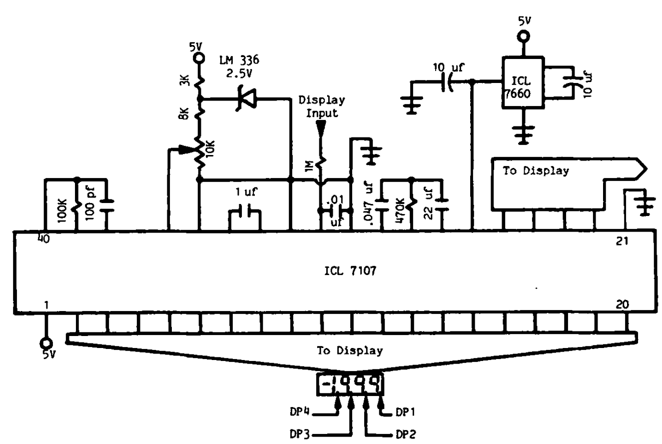


**Fig. 3. Display circuit for the organic volatile meter.**

*Sample Preparation for Headspace Analysis.* Approximately 100 g of peanut seed is adequate for a sample. The sample is comminuted with a Waring Model 33BL79 Blendor and a 1 qt. Waring Model 501110 stainless steel cup with a two piece vinyl lid (Waring Commercial, P. O. Box 207, New Hartford, CT 06057). The blender-cup lid is modified by removing the clear plastic centerpiece of the lid and gluing a 2.5 cm steel standard plate washer (2.8 cm ID x 6.2 cm OD x 0.4 cm thick) on the top center of the lid. A No. 7 rubber stopper is used to seal the opening in the washer. Preliminary studies indicate approximately 8 sec is required to properly comminute a 100 g sample of peanut seed. A Dayton Model No. 6X604C interval delay timer (W. W. Grainger, 2738 West Fulton St., Chicago, IL 60612) with a push-button switch is used to time the operation of the blender. After the sample is comminuted, the concentration of headspace volatiles is measured by removing the rubber stopper and immediately inserting the OVM probe to keep the blender cup sealed.

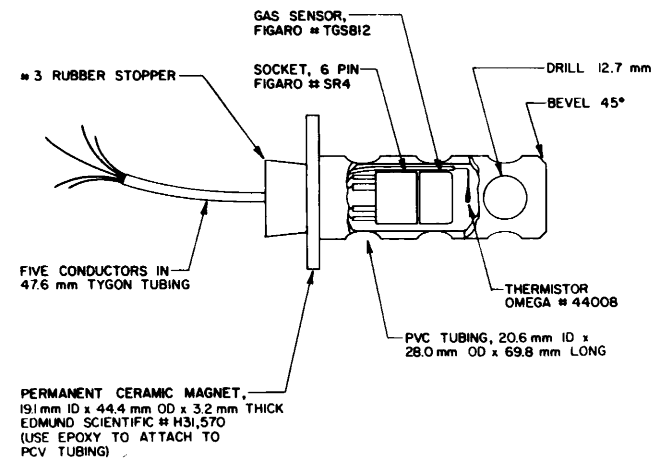


**Fig. 4. Sensor probe for the organic volatile meter.**

*Calibration and Standardization of the OVM.* Because each Taguchi sensor responds differently, a calibration curve for each OVM must be determined. To develop calibration curves, OVM readings were made in the headspace of the following concentrations of absolute ethyl alcohol in distilled water: 0.08 mL/L, 0.16 mL/L, 0.32 mL/L and 0.64 mL/L. These ethyl alcohol concentrations were used, because previous tests indicated that the range of OVM readings over these solutions includes the range of OVM readings over peanuts cured above 35 C or freeze damaged. The calibration solutions were prepared and stored in 7.6 L polypropylene jars (Cat. No. T5-6029-50, Cole Parmer Inst. Co., 7425 North Oak Park Ave., Chicago, IL 60648). A 2.8 cm hole was punched in the jar lids and sealed with No. 7 rubber stoppers. Four L calibration solutions were prepared by adding proper amounts of distilled water and absolute ethyl alcohol to the jars.

Hager *et al.* (3) published Eq. 1 and values of the Ostwald partition ratio (k) which can be used to compute the concentrations of ethyl alcohol vapor in the headspace over ethyl alcohol-water solutions. The Ostwald partition ratio (k) is a function of the temperature of the solution. After proper conversion of units, Eq. 1 may be written in the form of Eq. 2.

$$k = (\text{mg alcohol per L air})/(\text{mg alcohol per mL water}). \quad (1)$$

$$\text{mg alcohol per kg air} = 658.7\ k\ (\text{mL alcohol per L water}). \quad (2)$$

When the temperature of the alcohol-water solution is 21 C, k equals 0.167. Eq. 2 with this k value was used to compute the alcohol concentration (mg alcohol/kg of dry air) in the headspace over the four calibration solutions at 21 C. Two OVM were each standardized by adjusting the meter readings to 311 in the headspace over the 0.08 mL/L calibration solution and OVM readings were taken for the remaining 3 solutions. To obtain calibration curves, the meter readings and alcohol concentrations in the headspace over the calibration solutions were plotted on a semi-logarithmic graph.

*Procedure for Sample Analysis.* Standardize the OVM with the following procedure: (i) Insert the probe into the headspace of the 0.08 mL/L standardization solution and immediately activate the 45 sec timer (Fig. 2). (ii) At the buzzer, adjust the standardization resistor (Fig. 1) so the OVM reads 311. (iii) Adjust the 10 K temperature resistor (Fig. 1) until all of the warning lights are out. (iv) Remove the probe from the standardization solution jar, immediately replace the rubber stopper and return the probe to the holder on the meter box.

Put approximately 100 g of peanuts into the blender cup, seal the cup with the lid and activate the timer to comminute the peanuts for 8 sec. Remove the rubber stopper from the blender lid and insert the probe. Activate the 45 sec timer and read the OVM at the buzzer. Return the probe to the holder on the meter box, dump the comminuted sample from the blender cup and brush the cup clean. Allow about 1 min for the probe to equilibrate with laboratory conditions before reading the headspace in another sample. The OVM should be restandardized every 4 h or whenever DP1 or DP3 are lighted (Fig. 3).

*Performance of the OMV.* A series of tests was made to determine OVM readings for samples of peanuts with a known relative range of volatile organic compound concentrations. Comminuted freeze-damaged peanuts with a high volatile organic compound concentration were mixed with comminuted undamaged peanuts with a low volatile organic compound concentration to obtain five 200 g samples with one each of the following high/low ratios: Og/200g, 50g/150g, 100g/100g, 150g/50g and 200g/0g. Two OVM's were used to measure the organic volatile concentration in the headspace over each of the 5 samples. The test was replicated 4 times.

Three tests were made to determine the effect of drying on the volatile organic compound concentration in peanuts over the range of approximately 7% to 11% moisture within which farmers stock peanuts may be marketed. In Test 1, freshly harvested peanuts with approximately 40% moisture (wet basis) were freeze damaged by exposing them to -1 C for 8 h and then dried to 12.9% moisture content with 35 C forced air. For Test 2, peanuts harvested from the windrow with approximately 25% moisture content were dried to 12% moisture content with 50 C forced air. For Test 3, peanuts harvested from the windrow with approximately 25% moisture content were dried to 13% moisture content with 35 C forced air. After the initial drying treatments, the peanuts from all 3 tests were shelled and dried in a controlled chamber regulated at 29 C dry bulb and 21 C wet bulb. As the peanuts dried, 100 g samples of shelled peanuts were analyzed with the OVM. Three 100 g samples from each test were analyzed at each of 7 or more moisture contents within the range of 11.5% to 5.5% moisture content.

# Results and Discussion

Calibration curves for the two OVM's are shown in Fig. 5. When the alcohol concentration in the headspace was plotted on a logarithmic scale versus meter reading, a linear relationship was found for Meter 1, but the relationship for Meter 2 was not quite linear. Also, the slope of the curve was greater for Meter 1 than for Meter 2. These data demonstrate that a calibration curve is necessary for each OVM if the meter is to be used to measure a range of headspace concentrations.

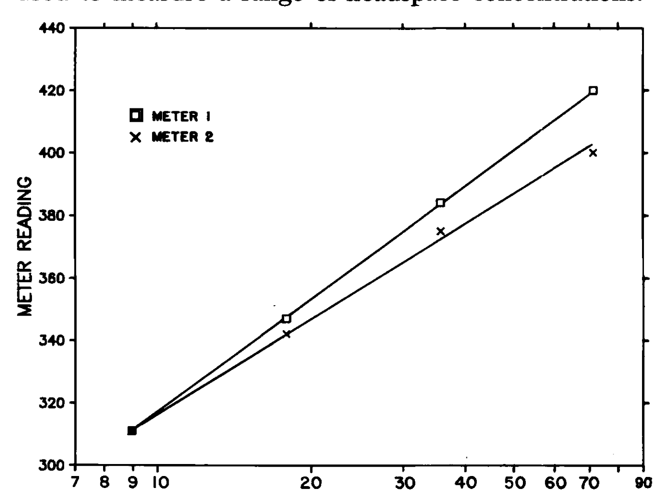


**Fig. 5. Calibration curves for two organic volatile meters.**

A plot of the concentrations of organic volatiles in the headspaces over samples of comminuted peanuts with known percentages of freeze-damaged peanuts in the samples is shown in Fig. 6. Each point is an average of one measurement on each of 4 samples. Measurements by both meters are approximately proportional to the percentage of freeze-damaged peanuts in the samples. (The sample with no freeze-damaged peanuts contained some organic volatiles). The deviation from a straightline relationship between the two parameters indicates that the proportionality between the headspace organic volatile concentration and the sample volatile organic compound concentration is not constant over the concentrations used in this test. In other words, Henry's law (10) which states "the mass of a slightly soluble gas that dissolves in a definite mass of liquid at a given temperature is very nearly directly proportional to the partial pressure of that gas" is not applicable for the range of volatile organic compound concentrations in these comminuted peanuts. Another explanation may be that the OVM calibration curve for headspace ethanol concentration (Fig. 5) is not completely accurate for headspace organic volatile concentrations of freeze-damaged peanuts. Nevertheless, OVM measurement of headspace organic volatile concentrations is a reasonably accurate method to classify samples of peanuts according to their relative concentrations of volatile organic compounds.

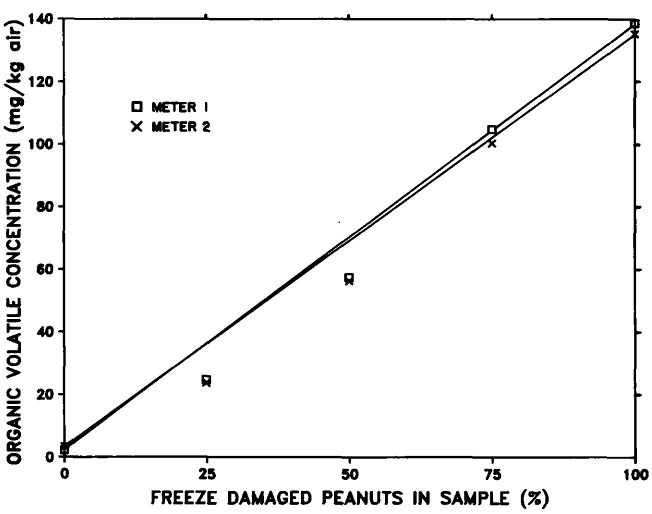


**Fig. 6. The relationship between the concentration of organic volatiles in the headspace and the percentage of freeze damaged peanuts in the sample.**

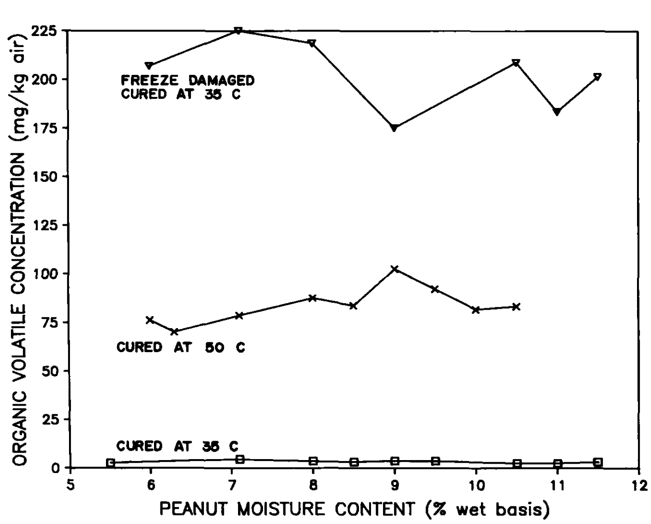


**Fig. 7. The effects of drying on the headspace organic volatile concentration of peanuts.**

The relationship between moisture content and headspace organic volatile concentration for 3 different peanut samples is shown in Fig. 7. Each point represents the average of one OVM measurement on each of three 100 g subsamples. These data indicate the effects of freeze damage and high-temperature-curing damage on the headspace organic volatile concentration of peanuts and that drying the peanuts from 11% to 6% moisture content has little or no effect on their organic volatile concentration.

The OVM described in this paper provides an objective method to classify comminuted samples of farmers stock peanuts according to the concentration of organic volatiles in their headspace. Additional unpublished studies by the authors have demonstrated that use of this procedure at the first point of sale makes it possible to classify farmers stock peanuts according to their concentration of objectionable flavors.

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