

A Novel Silica Gel Adsorption/Near-Infrared Spectroscopic Method for the Determination of Hexanal as an Example of Volatile Compounds

Hui-Zhen Zhang and Tung-Ching Lee*

Department of Food Science, the Center for Advanced Food Technology, and the Institute of Marine and Coastal Sciences, Cook College, Rutgers University, P.O. Box 231, New Brunswick, New Jersey 08903

The present research has demonstrated the feasibility of using silica gel adsorption/near-infrared (near-IR) reflectance spectroscopy to determine hexanal as an example of volatile compounds. Using a first-derivative mathematical treatment for the near-IR spectra of hexanal adsorbed on silica gel provides better results than the raw near-IR spectra. The wavelengths from 1650 to 1790 nm show a linear relationship between first-derivative near-IR reflectance and hexanal contents on silica gel. The two best simple linear regression equations [$Y_L = 7.89 \times 10^{-6} + 1.711 \times 10^{-4}(X_L)$; $Y_H = 4.319 \times 10^{-4} + 8.69 \times 10^{-5}(X_H)$] obtained from the regression equations of eight groups fit in lower hexanal contents ranging from 7.8 to 39 mg/10 g of Si and higher hexanal contents ranging from 39 to 546 mg/10 g of Si, respectively. The correlation coefficient between the near-IR-predicted value using the two equations and the added standard value of hexanal adsorbed on silica gel is 0.997. The relative errors were less than 9%.

Keywords: *Silica gel adsorption; near-infrared; hexanal; volatile compounds*

INTRODUCTION

The determination of trace volatile organic compounds is currently receiving increasing attention. This is because some trace volatile organic compounds (e.g., carbonyl compounds) are an important index not only for evaluating food quality but also for evaluating atmospheric pollution.

In food systems, lipid oxidation is one of the main deteriorating reactions related to the development of off-flavors in lipid rich foods (Fritsch et al., 1977; Min, 1981; Robards, 1988; Lubis et al., 1990; Nawar et al., 1990). A large number of volatile compounds, including aldehydes, ketones, alcohols, hydrocarbons, and other products, are formed during the oxidation of unsaturated fatty acids (Noble et al., 1971, 1975; Frankel et al., 1981, 1988; Ullrich et al., 1987, 1988). Linoleic acid, a predominant unsaturated fatty acid in many food products, can be oxidized to hexanal, octanal, and 2,4-decadienal which further decomposes into hexanal (Ullrich et al., 1987). These volatile compounds, especially hexanal, have been commonly used to gauge the extent of lipid oxidation and as a quality index for many food products. The odor threshold value of hexanal in cereal is approximately 0.15 ppm (Fritsch et al., 1977; Koelsch et al., 1991). Therefore, determination of volatile compounds (e.g., hexanal) as a quality index is very important.

Many methodologies developed for determining hexanal and other volatile compounds, such as gas chromatography (GC) and colorimetric methods, are complicated and tedious. Also, these methods are not easily adapted to on-line control. Consequently, it would be advantageous to develop a novel, rapid, simple, and accurate technique to determine hexanal and other volatile compounds.

Near-IR spectroscopy has been recognized as a powerful analytical technique and a widely used method for

the determination of various constituents in agricultural, food, and other products (Osborne et al., 1986; Williams et al., 1987; McClure, 1994). It is very rapid and nondestructive, with little or no sample preparation required. Furthermore, the near-IR spectroscopic method has a greater appeal because it does not use chemicals and cause environmental pollution like conventional analytical methods. The near-IR method has been developed to determine protein, fat, moisture, and carbohydrate in different foods because the traditional techniques to determine these components in food are laborious and time-consuming (Ben-Gera et al., 1968; Kruggel et al., 1981; Lanza, 1983; Davies et al., 1985; Kim et al., 1990; Mitsumoto et al., 1991; Lee et al., 1992; Isaksson et al., 1995; Zeng et al., 1996). Usually the contents of protein, fat, moisture, and carbohydrate as main components of foods are higher compared with hexanal and other volatile compounds. Due to the sensitivity of the near-IR method and the low concentration of hexanal and other volatile compounds, it is difficult to determine these compounds directly using the near-IR method without any concentrating step. Fong and Hieftje (1995) reported near-IR measurement of relative and absolute humidity through detection of water adsorbed on a silica gel layer. They used silica gel high-performance thin-layer chromatography (TLC) plates to adsorb water vapor and determine the water content in the TLC plates. Silica gel used here has two purposes: one is as a carrier of analyzed compounds; the other is as a concentrator. Volatile compounds have almost the same behavior as water vapor with regard to adsorption on silica gel. Therefore, if we could develop a near-IR method to determine volatile organic compounds, the near-IR spectroscopic method would have a much broader application.

The objective of the present study was to investigate the feasibility of using the silica gel adsorption/near-IR spectroscopic method to determine hexanal as an example of volatile compounds at trace levels.

* Author to whom correspondence should be addressed [tel, (908) 932-9611, ext. 236; fax, (908) 932-6776; e-mail, lee@aesop.rutgers.edu].

MATERIALS AND METHODS

Materials. Silica gel (12, 28/200 mesh) was obtained from Alltech Associates, Inc. (Deerfield, IL). Hexanal was obtained from Sigma Chemical Co. (St. Louis, MO).

Near-IR Spectroscopy Analysis. All near-IR measurements were made with a Model 6500 spectrophotometer (NIRSystems, Inc., Silver Spring, MD). This instrument contains a computer-based system with a single-scanning monochromator. The monochromator scans the range 1100–2500 nm in the reflectance mode. Data were recorded at 2-nm intervals, and 32 scans were averaged for every sample. A standard, round sample holder filled with 10 g of pure silica gel was used as a reference. The lead sulfide detector was used for reflectance measurements. Near-IR spectral processing was performed on an IBM-386 interactive computer system. Regression computations were performed with the NSAS statistical software system (NIRSystems, Perstorp Analytical Co., Silver Spring, MD).

Preparation of Samples for Near-IR Analysis. The test model used nitrogen gas (flow rate: 50 mL/min) to purge a specific amount of hexanal to 10 g of silica gel at a certain temperature and certain time. The 10 g of silica gel-adsorbed hexanal was poured into the sample holder for near-IR determination.

Statistical Analysis. All the statistical analyses were performed by using the statistical program in the SigmaPlot Software package (Jandel Scientific, San Rafael, CA).

RESULTS AND DISCUSSION

Purge and trap techniques are a means to separate volatile compounds from the food system. Food systems are usually very complicated. The main components, such as moisture, lipid, protein, and carbohydrate, always interfere with the determination of minor constituents, especially near-IR determination. In order to eliminate the effect of the food matrix and increase the sensitivity for the determination of minor constituents, we usually need to find some techniques to separate the minor compounds from the food system. Purge and trap was used for volatile compounds that can escape from the food matrix with purge gas and be trapped on the special adsorbents. In our research, the target was volatile compounds, such as hexanal. Therefore, we took advantage of the purge and trap techniques to perform our sample preparation for near-IR determinations. Nitrogen was chosen as the purge gas because it is cheap and inert (no adsorption on the adsorbent and no reaction with the food sample). Silica gel was chosen as the adsorbent because it is cheap (disposable) and can adsorb polar volatile compounds, such as hexanal.

Effects of Purge Time and Purge Temperature for Hexanal Adsorbed on Silica Gel. Hexanal is a volatile compound. Silica gel can adsorb hexanal under certain conditions. The purge time and purge temperature directly affected the efficiency of silica gel in adsorbing hexanal. Therefore, the purge time and purge temperature were very important parameters for silica gel to quantitatively adsorb hexanal. Either a shorter purge time or a lower purge temperature may cause the hexanal not to be able to be quantitatively purged from the food sample. Thus the amount of hexanal adsorbed on silica gel was lower than that in the food sample under these conditions. The longer purge time may cause the already adsorbed hexanal on the silica gel to be desorbed. In order for the total hexanal to be purged out and quantitatively be adsorbed on silica gel, we determined the near-IR reflectance of hexanal adsorbed on silica gel at purge times of 1, 2, and 4 h under a purge temperature of 90 °C and at a purge time of 1 h under purge temperatures of 80, 90,

Table 1. Effects of Purge Time and Purge Temperature for the Near-IR Reflectance of Hexanal Adsorbed on Silica Gel

purge time (h)	purge temperature (°C)				SD
	80	90	100	mean	
1	0.0338 ^a	0.0378	0.0366	0.0361	0.0021
2	0.0366	0.0360	0.0371	0.0366	0.0006
4		0.0365			
mean	0.0352	0.0368	0.0368		
SD	0.0019	0.0009	0.0004		

^a First-derivative near-IR reflectance values from triplicate determination of 234 mg of hexanal adsorbed on 10 g of silica gel.

and 100 °C. The results are shown in Table 1. We can see that the near-IR reflectance values of the hexanal adsorbed on silica gel at 90 °C for a purge time from 1 to 4 h were almost the same. The standard deviation (SD) of near-IR reflectance values for different purge times was 0.0009. Thus, the purge time was set for 1–1.5 h for our experiment.

The purge temperatures of 80, 90, and 100 °C for hexanal adsorbed on silica gel also were assessed by near-IR reflectance under purge times of 1 and 2 h. The near-IR reflectance value at 80 °C was lower than that at 90 and 100 °C when the purge time was set for 1 h. The near-IR reflectance values for the three temperatures were almost the same when the purge time was set for 2 h. The SD of the near-IR reflectance values for the three purge temperatures was 0.0006. Therefore, a purge time between 1 and 1.5 h and a purge temperature of 90 °C were selected for our experimental conditions. The boiling point of water at 1 atm is 100 °C. The purge temperature selected for hexanal adsorbed on silica gel was lower than the boiling point of water. This selection avoided some water evaporation to the silica gel, thereby reducing some of the water effect for hexanal adsorbed on silica gel. Also, we were able to eliminate the water vapor effect by passing the mixture of volatile compounds and water vapor through a desiccant, so that only the volatile compounds passed through the desiccant to be adsorbed on the silica gel. From the results of different purge times, we also found that we could extend the purge time to 4 h for low-hexanal-content food samples by simply increasing the amount of the testing sample. This would relatively increase the detectability for hexanal and other volatile compounds in food samples.

Mathematical Treatment for Raw Near-IR Spectral Data. Mathematical treatment is a modification of raw spectral data. The treatment can correct the baseline, enhance spectral data, or assist in smoothing a spectrum. Application of a mathematical treatment will prepare the raw spectral data for use in a regression and subsequent development of a calibration equation. The mathematical treatments of the spectra usually are *N*-point smoothing, first derivative, and second derivative. Figure 1 shows the raw near-IR spectra with different amounts of hexanal adsorbed on silica gel. From Figure 1, we can see that the baseline of each spectrum is different and disordered. We can not obtain any information about the relationship between hexanal content on silica gel and near-IR reflectance. Therefore, it was necessary to make some mathematical treatments of the spectra. We selected the first-derivative and second-derivative mathematical treatments to complete this task because the *N*-point smoothing only smoothed the spectra with no contribution to the baseline modification of the spectra. In this work, both the first derivative and the second derivative can eliminate

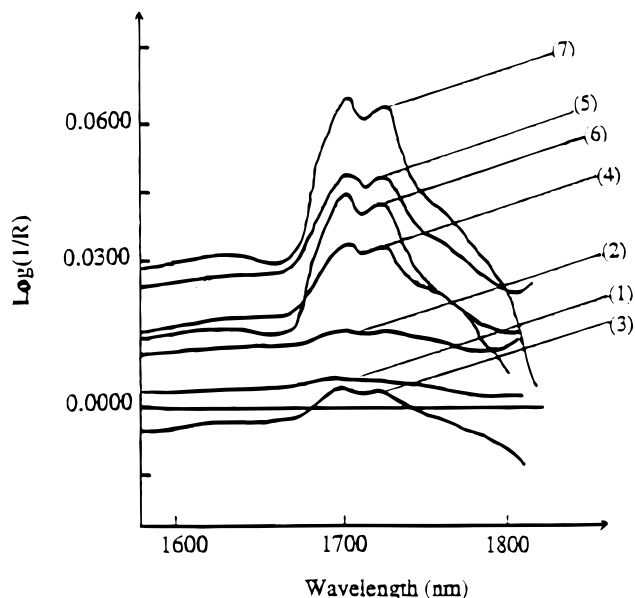


Figure 1. Raw near-IR spectra of hexanal with different concentrations adsorbed on silica gel. The hexanal concentrations (mg/10 g of Si) for each spectrum are as follows: (1) 7.8, (2) 15.6, (3) 39.0, (4) 78.0, (5) 234, (6) 390, (7) 546.

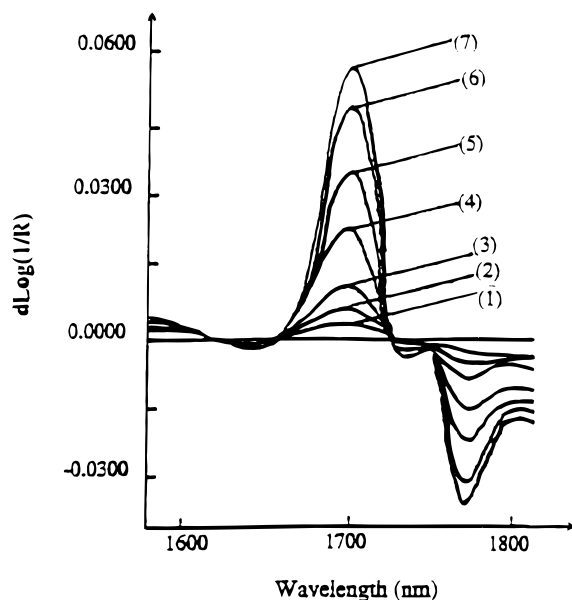


Figure 2. First-derivative near-IR spectra of hexanal with different concentrations adsorbed on silica gel. The hexanal concentrations (mg/10 g of Si) for each spectrum are as follows: (1) 7.8, (2) 15.6, (3) 39.0, (4) 78.0, (5) 234, (6) 390, (7) 546.

the effect of baseline drift of the spectra. However, the first derivative generally was given priority because the data from the first derivative was more stable than the data from the second derivative. Therefore, the first derivative was selected as the mathematical treatment of the spectra.

The results of the first derivative spectra (segment size 20 nm, gap size 5 nm) of different amounts of hexanal adsorbed on silica gel are shown in Figure 2 (corresponding to Figure 1). From Figure 2, we can see that the baseline variations are reduced, and the linear relationship between the hexanal content and the near-IR reflectance value from 1650 to 1790 nm is obviously exhibited. Thus, it was possible to directly determine the hexanal content that had adsorbed on silica gel.

Table 2. Repeatability and Reproducibility Test of Using Near-IR Reflectance for the Determination of Hexanal Adsorbed on Silica Gel within 1 and 20 Days

sample no.	1 day	20 days (4-day interval)
1	0.0573 ^a	0.0582
2	0.0570	0.0571
3	0.0580	0.0598
4	0.0596	0.0590
5	0.0591	0.0565
mean	0.0582	0.0581
SD	0.001125	0.001348
CV	1.93%	2.32%

^a First-derivative near-infrared reflectance values of 546 mg of hexanal adsorbed on 10 g of silica gel.

Repeatability and Reproducibility of Using Near-IR Reflectance for the Determination of Hexanal Adsorbed on Silica Gel. Repeatability and reproducibility are important parameters to evaluate new analytical methods. Therefore, it is necessary to determine these two parameters when new analytical methods are developed. Generally, repeatability is obtained in analyses carried out in one laboratory by one operator, using one piece of equipment over a relatively short time span. Reproducibility is defined as the long-term variability of the measurement process and may be determined for a method run within a single laboratory but on different days. Reproducibility also applies to a method run either by different operators, by different instruments, or by a combination of the above (Massart et al., 1978). The five time measurements of the near-IR reflectance for the hexanal adsorbed on silica gel during a short time span (within 1 day) and a longer time span (within 20 days at 4-day intervals) are shown in Table 2. The coefficients of variability (CV) and SD of near-IR reflectance for the short time span (repeatability) were 0.0193 and 0.001125. The CV and SD of near-IR reflectance for the longer time span (reproducibility) were 0.0232 and 0.001348. Both values for CV and SD were acceptable. Therefore, the use of near-IR reflectance for determination of the hexanal adsorbed on silica gel is stable and reliable.

Minimum Detectable Activity (MDA). There are many parameters that affect the MDA of the near-IR spectroscopic method, among these are instrument noise and the near-IR sensitivity of the instrument to hexanal and silica gel. In detecting the near-IR reflectance of pure silica gel several times, the results of the first-derivative near-IR reflectance were all found to be about in the order of 10^{-6} . The first-derivative near-IR reflectance for the minimum content of hexanal adsorbed on silica gel (78 mg/10 g of Si) was about in the order of 10^{-3} . It was far larger than that of the noise (10^{-6} order). Thus, our method can easily detect the hexanal content for more than 78 mg/10 g of Si.

Regression Equation of Hexanal Adsorbed on Silica Gel. From Figure 2, we had found that a linear relationship between hexanal content and first-derivative near-IR reflectance was exhibited. Therefore, we can establish a linear regression equation:

$$Y = K_0 + K_1(X) \quad (1)$$

where X is the hexanal content, Y is the first-derivative near-IR reflectance, and K_0 and K_1 are the constants of the regression equation. From this equation, we can directly and quantitatively determine hexanal content from the value of the first-derivative near-IR reflectance. Figure 2 shows that the maximum value of the first-

Table 3. Eight-Group Regression Constants for Hexanal Adsorbed on Silica Gel Using Near-IR Reflectance Spectroscopy

group no.	regression constants					
	K_{0T}^a	K_{1T}^a	K_{0L}^b	K_{1L}^b	K_{0H}^c	K_{1H}^c
1	2.52×10^{-4}	9.50×10^{-5}	1.56×10^{-5}	1.824×10^{-4}	5.363×10^{-4}	8.79×10^{-5}
2	2.21×10^{-4}	9.61×10^{-5}	-1.04×10^{-5}	1.850×10^{-4}	5.061×10^{-4}	8.90×10^{-5}
3	1.80×10^{-4}	9.68×10^{-5}	-5.23×10^{-6}	1.655×10^{-4}	4.188×10^{-4}	9.08×10^{-5}
4	1.59×10^{-4}	9.90×10^{-5}	-1.91×10^{-6}	1.519×10^{-4}	3.790×10^{-4}	9.36×10^{-5}
5	1.78×10^{-4}	9.84×10^{-5}	2.21×10^{-5}	1.726×10^{-4}	3.990×10^{-4}	9.29×10^{-5}
6	1.61×10^{-4}	8.48×10^{-5}	2.46×10^{-5}	1.730×10^{-4}	3.908×10^{-4}	7.92×10^{-5}
7	2.31×10^{-4}	8.92×10^{-5}	7.08×10^{-6}	1.702×10^{-4}	4.213×10^{-4}	8.45×10^{-5}
8	1.99×10^{-4}	8.23×10^{-5}	7.44×10^{-6}	1.668×10^{-4}	4.044×10^{-4}	7.72×10^{-5}
mean	1.98×10^{-4}	9.27×10^{-5}	7.89×10^{-6}	1.711×10^{-4}	4.319×10^{-4}	8.69×10^{-5}
SD	0.34×10^{-4}	0.64×10^{-5}	1.24×10^{-5}	1.06×10^{-5}	5.74×10^{-5}	6.09×10^{-6}

^a The regression constants for hexanal contents ranging from 7.8 to 546 mg/10 g of Si. ^b The regression constants for hexanal contents ranging from 7.8 to 39 mg/10 g of Si. ^c The regression constants for hexanal contents ranging from 39 to 546 mg/10 g of Si.

derivative near-IR reflectance for hexanal adsorbed on silica gel is at the wavelength of 1690 nm. Therefore, 1690 nm was selected as a regression wavelength. According to the principle of statistics, we knew that K_0 and K_1 were random variables taken independently from different group samples. If we used a regression equation obtained from only one group sample to predict the unknown samples, the data will be unstable and unreliable. Therefore, to obtain more stable regression equations for the precise prediction of the unknown samples, we should determine several group samples and find the corresponding regression equations. From these regression equations, we can establish a new regression equation:

$$Y = \bar{K}_0 + \bar{K}_1(X) \quad (2)$$

where $\bar{K}_0 = 1/n(K_{01} + K_{02} + \dots + K_{0n})$, $\bar{K}_1 = 1/n(K_{11} + K_{12} + \dots + K_{1n})$, and n is the number of group samples. Therefore, using the new regression eq 2 was more logical.

In this paper, from the eight group samples, we obtained eight regression equations, respectively. The K_0 and K_1 values are shown in Table 3. Using the means of K_0 and K_1 obtained from the eight regression equations, we established a new regression equation:

$$Y = 1.976 \times 10^{-4} + 9.27 \times 10^{-5}(X) \quad (3)$$

However, when we used this new eq 3 for the prediction of the hexanal adsorbed on silica gel, the results showed bigger relative errors compared with the standard value (Table 4). The reason for this was that the linear trend between lower hexanal contents and higher hexanal contents was different. However, the results were obviously improved when the data were divided into two ranges (lower hexanal contents and higher hexanal contents) for the use of separate regression. Table 3 also shows the eight-group regression constants for the two ranges of hexanal contents. We therefore obtained two regression equations that fit the lower hexanal contents and the higher hexanal contents, respectively. The regression equation can be expressed as:

$$Y_L = 7.89 \times 10^{-6} + 1.71 \times 10^{-4}(X_L) \quad (4)$$

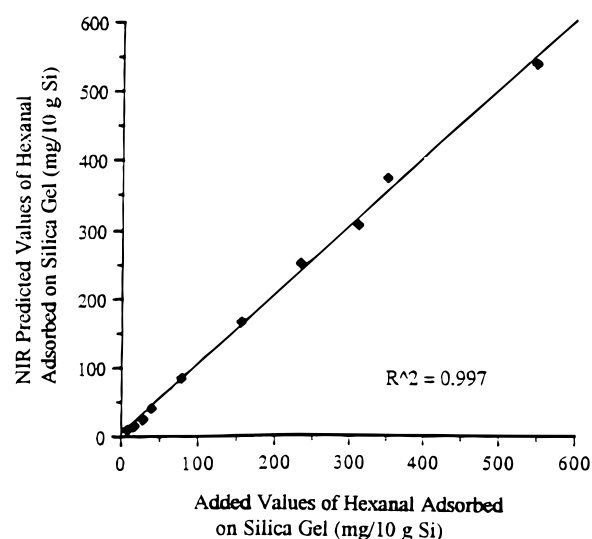
$$Y_H = 4.32 \times 10^{-4} + 8.69 \times 10^{-5}(X_H) \quad (5)$$

where eq 4 is suitable for hexanal contents ranging from 7.8 to 39 mg/10 g of Si and eq 5 is suitable for hexanal contents ranging from 39 to 546 mg/10 g of Si.

Table 4. Near-IR-Predicted Values of Hexanal Adsorbed on Silica Gel from the Regression Eqs 3–5 in Comparison with the Added Standard Value of Hexanal

sample no.	hexanal contents (mg/10 g of Si)			RE ₁ (%) ^d	RE ₂ (%) ^e
	X_{add}^a	$X_{predict1}^b$	$X_{predict2}^c$		
1	7.8	-5.5	8.1		4
2	15.6	9.8	16.4	-46	5
3	39.0	51.8	39.0	28	0
4	27.3	26.0	25.2	-3	-8
5	78.0	105.2	85.3	40	9
6	156.0	180.6	165.7	15	6
7	312.1	311.2	305.0	-0.3	-2
8	351.1	376.3	374.5	7	6
9	234.0	258.4	249.0	10	6
10	546.1	529.0	537.0	-3	-2

^a The added values (standard) of hexanal adsorbed on silica gel. ^b The near-IR-predicted values of hexanal adsorbed on silica gel from the regression eq 3, hexanal contents ranging from 7.8 to 546 mg/10 g of Si. ^c The near-IR-predicted value of hexanal adsorbed on silica gel from the regression eqs 4 and 5, hexanal contents ranging from 7.8 to 39 and from 39 to 546 mg/10 g of Si, respectively. ^d The relative errors of $X_{predict1}$ compared with X_{add} . ^e The relative errors of $X_{predict2}$ compared with X_{add} .

**Figure 3.** Correlation between the near-IR-predicted values and added values of hexanal adsorbed on silica gel.

Prediction of Hexanal Contents on Silica Gel Using Obtained Regression Equations. We can use the above equations to predict the hexanal content when we know the value of the first-derivative near-IR reflectance of the hexanal adsorbed on silica gel. Figure 3 shows the high correlation (0.997) between the near-IR-predicted values and added standard values of hexa-

nal on silica gel. Table 4 shows the near-IR-predicted values of hexanal adsorbed on silica gel by using the regression eqs 4 and 5 in comparison with added standard values of hexanal. The results indicated that the relative error (RE₂) for each sample was less than 9% which was in the range of relative errors of instrumental methods.

Also we used the above method to determine pentanal, another lipid oxidation product. The results we obtained were the same as those for hexanal.

CONCLUSIONS

The results presented here, using a model system of silica gel to adsorb hexanal as an example of the volatile compounds, demonstrated the feasibility of determining volatile compounds (e.g., hexanal) at trace levels by the fast, simple near-IR spectroscopic method combined with silica gel adsorption. Silica gel as an adsorbent and a carrier was used here to improve the sensitivity of near-IR spectroscopy for trace-level compounds. It made the near-IR spectroscopy much more broadly applicable. The use of near-IR spectroscopy combined with silica gel and/or other adsorbents for food materials is the topic of an upcoming investigation.

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Received for review May 23, 1997. Accepted May 30, 1997.® This is publication D-10114-6-97 of the New Jersey Agricultural Experiment Station and the Institute of Marine and Coastal Sciences, Rutgers University, supported partially by the State Funds and Hatch Project and partially by the Rutgers/NOAA Cooperative Marine Education and Research (CMER) Program.

JF970440I

® Abstract published in *Advance ACS Abstracts*, July 15, 1997.