

# Simple Method for Estimation of Volatile Carbonyl Compounds in Edible Oils and Fried Potato Chips

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A simple and sensitive method has been devised to determine the amounts of volatile carbonyl compounds in vegetable oils and fried potato chips, using a chemical reaction trap and absorption spectrophotometry. A sample of oil or fried potato chips is heated and simultaneously purged with a flow of nitrogen gas which further bubbles through a tube (trap) containing a hydroxylamine hydrochloride solution. The volatile carbonyl compounds are removed from the sample with the purge gas and retained in the trapping solution as they react to form the less volatile oxime derivatives. These are subsequently estimated by ultraviolet absorption, at wavelength 212 nm for the total oximes and at 272 nm specifically for conjugated diene carbonyl oximes, including furfural if present. Volatile carbonyls can be determined by this method at levels as low as 0.1–0.5 ppm of the sample. The method has been applied to the analysis of samples of canola (low erucic acid rapeseed) oil, cottonseed oil, and potato chips, all before and after storage. The method should be suitable also for other types of fried food.

Various carbonyl compounds are formed by lipid autoxidation and subsequent degradation of the hydroperoxides. These compounds are of great significance in the odor of lipid-containing food products (1–3). Many techniques have been developed to analyze volatile compounds in oils and fried foods, using gas chromatography or absorption spectrophotometry. Gas chromatographic flavor profiles are generally very complex, however, and tend to be of limited value for quality evaluation of oils and other food products unless individual components are identified (4,5). A simple spectrophotometric method for determination of volatile carbonyl compounds in microbial metabolites has earlier been reported (6). The present paper describes the adaptation of this method for the determination of volatile carbonyl compounds in frying oils and in deep-fried potato chips.

## MATERIALS AND METHODS

**Principle of method.** The sample to be analyzed is heated and purged with a stream of nitrogen gas. The nitrogen stream, containing the volatile components purged from the sample, further bubbles through an aqueous solution of hydroxylamine-HCl, where the carbonyl compounds in the stream will react with the hydroxylamine to form oxime derivatives; these are relatively non-volatile and will thus be retained (trapped) in the solution. The amount of oximes in the solution is subsequently estimated by ultraviolet absorption spectrophotometry.

**Method.** A chemical reaction trap and two sample containers were designed—one for liquid samples (oil) and one for solid samples (potato chips) (Fig. 1). For analysis, a

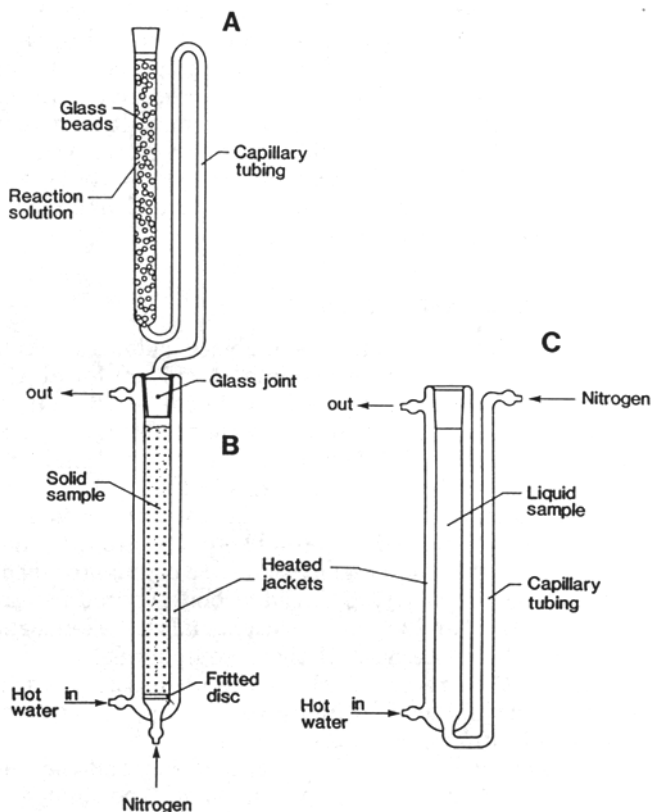


FIG. 1. Schematic diagram (scale 1:3) of apparatus for analyzing volatile carbonyl compounds. (A) Chemical reaction trap, (B) solid sample container, (C) liquid sample container.

sample of oil (25 ml) or lightly crushed potato chips (15 g) is placed in the appropriate container. The trap, containing 5 ml of a 10% (w/w) aqueous solution of hydroxylamine hydrochloride, is attached on top of the container. The container is heated with circulating water (85°C), and the sample is simultaneously purged with nitrogen gas (80 ml/min, 2 hr). The trapping solution is then poured into a 10-ml measuring cylinder, the trap is rinsed with distilled water, and the combined solutions are made up to 7-ml volume. The absorption spectrum for this solution is recorded from 200 to 340 nm, using an appropriate blank solution. The absorption maxima at 212 nm (oximes of aldehydes and ketones in general) and at 272 nm (conjugated diene carbonyl oximes, including furfural if present) are used in the calculation of results.

As calibration standards for determination of the wavelengths and extinction coefficients for the absorption maxima, samples of n-hexanal (Chem Service), furfural (Fisher), 1-octen-3-one (Sigma), 3-octanone (Fluka), and 2-hexenal, 2-octenal, 2,4-decadienal and 2,4-dodecadienal (Alfa Products Inc.) were analyzed in concentrations of 1–10 ppm. The sensitivity of the method was adjusted by varying the sample size and the volume of the trapping solution.

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**Materials.** Industrially refined and deodorized rapeseed oil (canola type) and cottonseed oil ("fresh oils"), obtained from Hostess Food Products Ltd., Cambridge, Ontario, were analyzed for volatile carbonyl compounds. Citric acid, but no antioxidants, had been added to the oils. Batches of potato chips were fried in the two oils in a laboratory fryer (185°C, 15 min) for a total of 20 hr of frying. The potato chips (pooled from all the fryings) and the "used oils" were stored at room temperature for 30 days in the dark or under fluorescent light, and analyzed for volatile carbonyl compounds before and after storage. Samples of the original (fresh) canola and cottonseed oils were deodorized in the laboratory for 20 hr at 100°C and 10<sup>-5</sup> torr; these "re-deodorized oils" were also analyzed for volatile carbonyl compounds.

## RESULTS AND DISCUSSION

The absorption spectra for the analyzed calibration standards showed absorption maxima at 212 nm for all the compounds tested, and an additional peak at 264 nm for the alkadienals, and at 274 nm for furfural (Fig. 2). Mixtures of furfural with 2,4-decadienal or 2,4-dodecadienal (oximes) gave only one peak in the 264–274 nm region, with the maximum at 272 nm. The absorption peak at 212 nm is due to the aldoxime and ketoxime groups, while that in the 264–274 nm region is due to a conjugated diene carbonyl oxime group (7,8). An additional absorption peak which appeared at 234 nm for the alkenals (2-hexenal and 2-octenal), characteristic of these compounds, was not utilized in the present work as the absorption at this wavelength diminished rapidly with time—probably as a result of an oximation process (9).

The recovery and precision of analysis by this method were estimated by analyzing n-hexanal, 2-hexenal, 2,4-decadienal, and furfural added to canola oil and potato chips (Table 1). The recoveries for the different samples

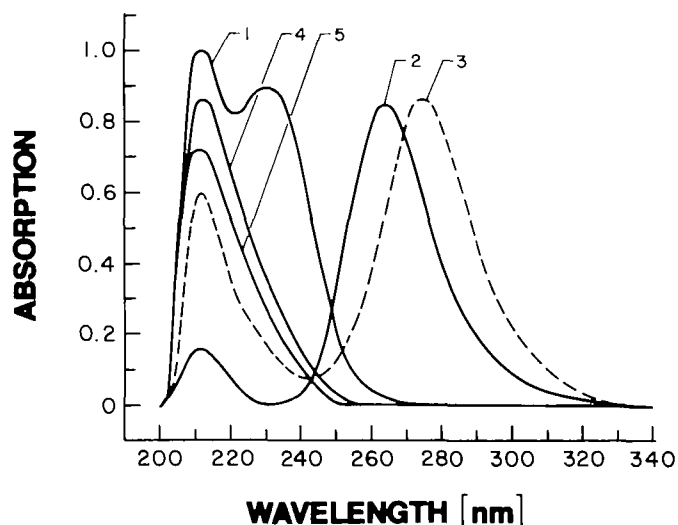


FIG. 2. Ultraviolet absorption spectra of the oximes of standard compounds. (1) 2-Hexenal and 2-octenal, (2) 2,4-decadienal and 2,4-dodecadienal, (3) furfural, (4) 1-octen-3-one, (5) 3-octanone and n-hexanal.

and concentrations ranged from 67.0% to 89.5%. The coefficient of variation for replicate analyses ranged from 3.0% to 5.1%. These recoveries and this precision of analysis are considered sufficient for obtaining comparative estimates of the volatile carbonyl compounds for different samples of oils and fried foods. Accurate determinations cannot be achieved by this method, however, since a mixture of oximes with different extinction coefficients is estimated by one single absorption peak (Table 2). The recovery experiments also indicated that the method can be used for analysis of relatively labile unsaturated carbonyl compounds, such as 2,4-decadienal,

TABLE 1

Recovery and Precision of Analysis for Aldehydes Added to Canola Oil and Potato Chips<sup>a</sup>

Standard	Canola oil				Potato chips																												
	Added (ppm)	Recovery (ppm)	Recovery (%)	CV <sup>b</sup> (%)	Added (ppm)	Recovery (ppm)	Recovery (%)	CV <sup>b</sup> (%)																									
Hexanal	0.5	0.39	77.9	4.8	1.0	0.81	80.9	4.7	10.0	8.82	87.8	3.1	0.5	0.39	77.9	4.9	1.0	0.78	78.4	3.9	10.0	8.27	86.3	3.8									
	10.0	8.82	87.8	3.1	10.0	8.82	87.8	3.1	10.0	8.82	87.8	3.1	10.0	8.27	86.3	3.1	10.0	8.27	86.3	3.8	10.0	8.27	86.3	3.8									
	100.0	87.8	87.8	3.1	100.0	87.8	87.8	3.1	100.0	87.8	87.8	3.1	100.0	82.7	86.3	3.1	100.0	82.7	86.3	3.8	100.0	82.7	86.3	3.8									
	100.0	87.8	87.8	3.1	100.0	87.8	87.8	3.1	100.0	87.8	87.8	3.1	100.0	82.7	86.3	3.1	100.0	82.7	86.3	3.8	100.0	82.7	86.3	3.8									
2-Hexenal	0.5	0.41	82.0	3.9	1.0	0.88	88.0	4.1	10.0	8.78	87.8	3.2	0.5	0.42	84.0	4.1	1.0	0.80	80.0	4.0	10.0	8.48	88.2	4.0									
	10.0	8.78	87.8	3.2	10.0	8.78	87.8	3.2	10.0	8.78	87.8	3.2	10.0	8.48	88.2	3.2	10.0	8.48	88.2	4.0	10.0	8.48	88.2	4.0									
	100.0	87.8	87.8	3.2	100.0	87.8	87.8	3.2	100.0	87.8	87.8	3.2	100.0	84.8	88.2	3.2	100.0	84.8	88.2	4.0	100.0	84.8	88.2	4.0									
	100.0	87.8	87.8	3.2	100.0	87.8	87.8	3.2	100.0	87.8	87.8	3.2	100.0	84.8	88.2	3.2	100.0	84.8	88.2	4.0	100.0	84.8	88.2	4.0									
2,4-Decadienal	0.1	0.067	67.0	5.1	0.2	0.135	67.5	4.8	2.0	1.41	70.5	4.4	4.0	2.77	69.3	4.1	0.1	0.145	72.5	4.6	0.2	0.152	76.0	4.2	2.0	1.52	76.0	4.2	4.0	2.84	4.2	4.0	4.2
	2.0	1.41	70.5	4.4	2.0	1.41	70.5	4.4	2.0	1.41	70.5	4.4	2.0	1.41	70.5	4.4	2.0	1.41	72.5	4.6	2.0	1.52	76.0	4.2	2.0	1.52	76.0	4.2	4.0	2.84	4.2	4.0	4.2
	4.0	2.77	69.3	4.1	4.0	2.77	69.3	4.1	4.0	2.77	69.3	4.1	4.0	2.77	69.3	4.1	4.0	2.77	72.5	4.6	4.0	2.84	71.0	4.2	4.0	2.84	71.0	4.2	4.0	2.84	4.2	4.0	4.2
	4.0	2.77	69.3	4.1	4.0	2.77	69.3	4.1	4.0	2.77	69.3	4.1	4.0	2.77	69.3	4.1	4.0	2.77	72.5	4.6	4.0	2.84	71.0	4.2	4.0	2.84	71.0	4.2	4.0	2.84	4.2	4.0	4.2
Furfural	0.1	0.08	80.1	4.9	0.2	0.16	80.0	5.1	2.0	1.69	84.9	3.4	4.0	3.25	81.3	3.0	0.1	0.16	80.0	4.8	0.2	0.168	84.1	3.7	2.0	1.68	84.1	3.7	4.0	3.58	3.7	4.0	3.7
	2.0	1.69	84.9	3.4	2.0	1.69	84.9	3.4	2.0	1.69	84.9	3.4	2.0	1.69	84.9	3.4	2.0	1.69	80.0	4.8	2.0	1.68	84.1	3.7	2.0	1.68	84.1	3.7	4.0	3.58	3.7	4.0	3.7
	4.0	3.25	81.3	3.0	4.0	3.25	81.3	3.0	4.0	3.25	81.3	3.0	4.0	3.25	81.3	3.0	4.0	3.25	80.0	4.8	2.0	1.68	84.1	3.7	2.0	1.68	84.1	3.7	4.0	3.58	3.7	4.0	3.7
	4.0	3.25	81.3	3.0	4.0	3.25	81.3	3.0	4.0	3.25	81.3	3.0	4.0	3.25	81.3	3.0	4.0	3.25	80.0	4.8	2.0	1.68	84.1	3.7	2.0	1.68	84.1	3.7	4.0	3.58	3.7	4.0	3.7

<sup>a</sup>Corrections were made for blank values obtained with the pure oil and chips samples.

<sup>b</sup>Coefficient of variation, based on 10 replicate analyses.

## VOLATILE CARBONYL COMPOUNDS IN FRIED FOODS

TABLE 2

Molar Extinction Coefficients for Carbonyl Compounds Analyzed by Different Methods

Reagent and compound	Absorption maximum (nm)	Molar extinction coefficient	
TBA + malondialdehyde <sup>a</sup>	532	159,200	
	305	11,200	
	243	23,000	
Benzidine acetate <sup>b</sup> + heptanal	350	1,370	
	+ 2-nonenal	350	8,000
	+ 2,4-hexadienal	350	15,500
2,4-DNPH <sup>c</sup>	+ hexanal	430	18,700
	+ 2,4-hexadienal	263	32,800
Hydroxylamine <sup>d</sup>	+ hexanal	212	3,960
	+ octenal	212	4,150
	+ 2-hexenal	212	5,330
	+ 2,4-decadienal	268	27,270
	+ furfural	274	20,790

<sup>a</sup> Ref. (10).<sup>c</sup> Ref. (12).<sup>b</sup> Ref. (11).<sup>d</sup> The present work.

which apparently had not earlier been achieved (4). The method appears to be of only intermediate sensitivity relative to some other spectrophotometric methods for carbonyl determination, as indicated by the listed extinction coefficients (Table 2). However, the method is simple and easy to use and does not require sophisticated equipment or sample preparation.

The method was applied to the analysis of fresh and used canola and cottonseed oils as well as potato chips that had been fried in these oils; the used oils and the chips were analyzed before and after storage with and without light. The freshly re-deodorized oils were also analyzed (Fig. 3, Table 3). No volatile carbonyls were detected in the freshly re-deodorized canola and cottonseed oils. List *et al.* (13), however, indicated the presence of carbonyl compounds (not necessarily volatile) in industrially deodorized soybean oil, based on the anisidine test. Our industrially deodorized canola and cottonseed oils ("fresh oils") contained a small amount of total volatile carbonyls, but no detectable dienes. After 20 hr frying of potato chips in these oils, the amount of total carbonyls had increased, in the canola oil particularly, and a small amount of dienes had developed in this oil. As expected, the amount of total carbonyls further increased during storage of the used oils, particularly during storage under light. The dienes for the two oils, however, did not increase in the same consistent pattern, possibly because these particular compounds might have undergone secondary reactions during the period of storage (1).

The freshly fried potato chips contained somewhat higher concentrations of total carbonyls than found in the used oils, again with an inconsistent pattern for the dienes. The amount of total carbonyls and dienes in the chips tended to increase during storage, particularly in the presence of light. With potato chips having an oil content of perhaps 40%, all the carbonyl concentrations quoted for potato chips (Table 3) would be 2.5 times higher if calculated on the basis of the oil weight rather than the entire chip weight. It is reasonable, however, to find these higher concentrations in the chip oil than in

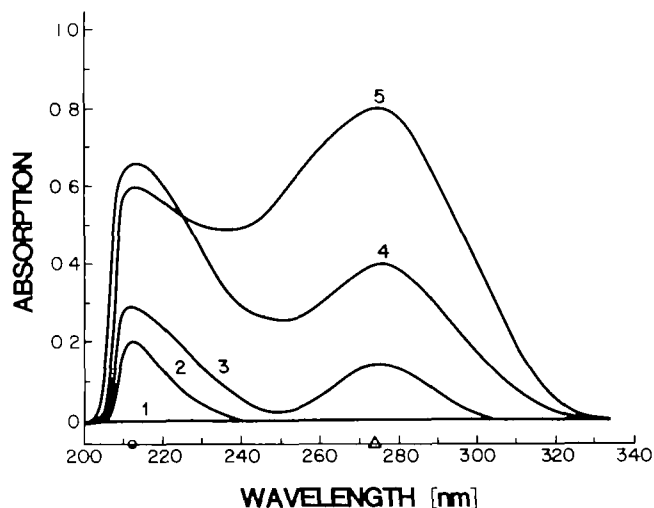


FIG. 3. Absorption spectra of the volatile carbonyl compounds trapped as oximes from (1) re-deodorized canola oil, (2) fresh canola oil, (3) used canola oil (i.e., fresh oil used 20 hr for frying of potato chips), (4) potato chips freshly fried in canola oil, (5) fried potato chips stored 30 days at room temperature under light. Fifteen grams of samples 1-4 were used in the analyses, but only 3 g of sample 5.

TABLE 3

Volatile Carbonyl Compounds in Canola and Cottonseed Oils and in Potato Chips Fried in These Oils<sup>a</sup>

Sample	Canola		Cottonseed	
	Total carbonyls <sup>b</sup>	Diene carbonyls <sup>c</sup>	Total carbonyls	Diene carbonyls
	mg/100 ml oil			
Re-deodorized oil <sup>d</sup>	0.0	0.0	0.0	0.0
Fresh oil <sup>e</sup>	1.78	0.0	1.08	0.0
Used oil <sup>f</sup>	3.14	0.21	1.10	0.01
Stored used oil (dark) <sup>g</sup>	4.22	0.29	1.58	0.03
Stored used oil (light) <sup>g</sup>	5.45	0.21	3.20	0.04
	mg/100 g chips			
Potato chips (fresh) <sup>h</sup>	4.50	0.12	3.80	0.10
Stored chips (dark) <sup>g</sup>	5.21	0.26	3.80	0.10
Stored chips (light) <sup>g</sup>	22.1	0.94	10.20	0.13

<sup>a</sup> Means of five replicate analyses. See Table 1, footnote b, concerning precision of analysis.

<sup>b</sup> Total volatile carbonyl compounds, expressed as n-hexanal.

<sup>c</sup> Total volatile diene carbonyl compounds (including furfural if present), expressed as 2,4-decadienal.

<sup>d</sup> Not used in frying.

<sup>e</sup> As received, before being used for frying.

<sup>f</sup> Used 20 hr for frying of potato chips.

<sup>g</sup> Stored 30 days at room temperature.

<sup>h</sup> Freshly fried in the fresh canola oil or cottonseed oil.

the bulk frying oil, as the chip oil is distributed over a large potato surface and thus should be more exposed to oxygen uptake and oxidation.

In comparing the canola oil with the cottonseed oil, and also the chips fried in canola oil with the chips fried in cottonseed oil, the total carbonyl and the diene concentrations were in every set of data higher for the canola oil and for the chips fried in this oil (Table 3). This more rapid oxidation or deterioration of the canola oil may be explained, in part, by the higher levels of linolenic acid (canola, 8.7%; cottonseed, 0.4%) and pigments in this oil (1,2).

The analyses and conclusions made in this report are not intended as an exhaustive study of the frying quality of the two oils used, but rather as an indication that the described method for analysis of volatile carbonyl compounds is simple and reproducible and appears promising as a tool for studying the quality of frying oils and fried foods.

#### ACKNOWLEDGMENTS

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