RESTEK
food & flavors

#59348

Applicationsnote

Monitoring Volatile Compounds in Food Contact Packaging Using Purge and Trap GC/MS and an Rtx®-5MS Capillary Column

Introduction

Food packaging can be designed from a wide variety of materials, in a range of sizes, shapes, and colors. With the increasing popularity of convenience foods, meals often are prepared within the packaging materials. Packages might be placed in an oven, a microwave, or within a pot of boiling water. For microwavable packaging, food manufacturers prefer to use cheap, safe, and, to some extent, recyclable materials.[1] Microwave susceptor systems can be used to heat foods more rapidly, as well as to crisp and brown the foods they contact. Susceptors are made by laminating metallized polyester to paperboard. For dual-ovenable applications, ovenable paperboard and CPET (crystalline polyethylene terephthalate) can be used.

For all packaging materials, there is the potential to generate undesirable volatile compounds when used at elevated temperatures. In many instances, these compounds can migrate into or out of packaging materials. When flavor compounds migrate out of a food or beverage into the packaging, scalping occurs. This can result in a loss of flavor or a change to the flavor profile. Of more concern from a food safety perspective are compounds that have the potential to migrate out of the packaging material into the food product.

The US Food & Drug Administration (FDA) has stated, “Anyone manufacturing food contact articles for use in the home or in food service establishments should make sure that nothing from the articles imparts flavor, color, odor, toxicity, or other undesirable characteristics to food, thereby rendering the food adulterated.”[2] In order to test the safety of food contact materials, packaging should be tested under simulated use conditions. Purge and trap gas chromatography/mass spectrometry (GC/MS) is a powerful tool for monitoring the volatile compounds that are generated during heating of packaging materials. This analysis technique can be applied to a wide range of packaging materials that are heated during food preparation.

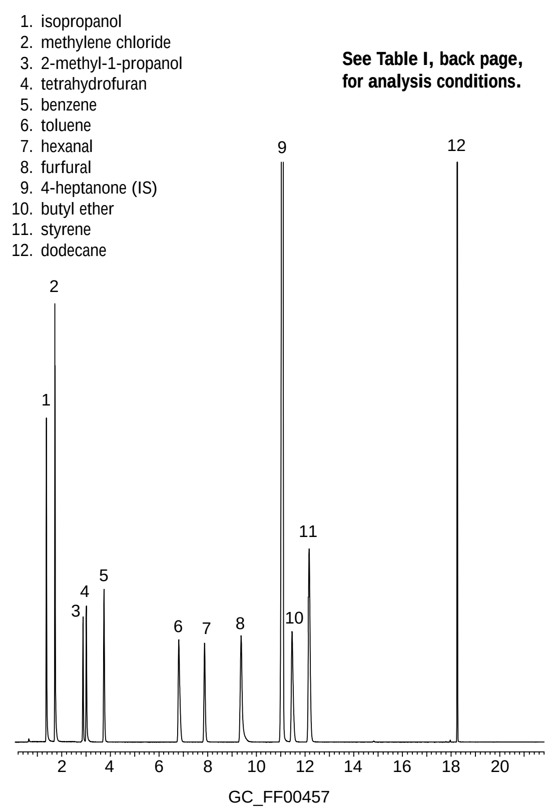
Indirect food additives are defined as substances that are used in the processing, packaging, holding, and/or transporting of food, have no functional effect on the food, but which might become a component of the food.[1] Plastic packaging in general is made of non-volatile, high molecular weight polymers, but volatile compounds often are added to improve the functional properties of the polymers. Such volatile compounds include plasticizers, antioxidants, UV blockers, and lubricants. The packaging inks and dyes used to create the label graphics can contain residual solvents, which may be toxic at certain concentrations. In addition, thermal breakdown of a polymer might occur in the inner ply of a boil-in bag or oven bag, thereby forming volatile species. Compounds such as benzene, styrene, and tetrahydrofuran (THF) have been shown to cause adverse affects on humans, and food contact materials need to be tested to ensure these volatiles are not present at significant levels.

In addition to the safety concerns, volatile compounds migrating into food materials can change the flavor profile of the food product. For example, polystyrene is used to package many aqueous-based, fatty or dry foods. Trace levels of styrene present in the polystyrene can impart a “plastic” taste to the food product.

In 21 CFR 170.39, the US FDA outlines the data needed to request an exemption from regulation as a food additive. Information needed includes the use conditions, time/temperature, food type, and whether the material is used once or multiple times. Other required information includes a detailed description of the analytical method and the method validation data, including the detection limit.

Figure 1

The Rtx®-5MS column exhibits good peak shape and high sensitivity for 12 volatile compounds that may be present in food packaging.



food & flavors

The FDA has defined two approaches to testing food contact materials: migration studies versus residual studies. In migration studies, food-simulating solvents are used to model the amount of material that migrates into the product. This is performed under worst-case, intended-use conditions. Changes in the food or ingredients used, such as a change in the fat content, can affect the migration of compounds out of the packaging material. For this reason, it is important to test the packaging under simulated use conditions to determine real-life effects on the food product.[3]

Residual studies estimate a worst-case dietary concentration level, assuming 100% migration of any volatiles generated into the food product. In residual studies, the level of each substance is measured in the finished food-contact article. If nothing is detected in the sample, then the validated detection limit can be used to estimate the dietary concentration.

While there are specific methods available for monitoring volatile compounds in defined systems, method development and validation often is the responsibility of the analyst. American Society for Testing and Materials (ASTM) Methods[4] F1308-98 and F1519-98 are qualitative and quantitative procedures (respectively) for monitoring the volatiles generated by microwave susceptor systems. Volatile extractables are defined as substances released from the susceptor and detected in the headspace. It is important to note that extractability does not necessarily mean migration to the food. ASTM F1308-98 is a quantitative procedure in which the packaging materials are heated in a sealed system within a microwave prior to drawing a headspace sample and injecting it into a GC/MS system. ASTM F1519-98 is a qualitative procedure for identifying the volatiles generated during simulated use conditions. This procedure uses a purge and trap apparatus to collect and concentrate the volatile compounds. These methods were used to develop the general procedure for testing volatiles in food contact packaging as described in this application note.

Experimental Conditions

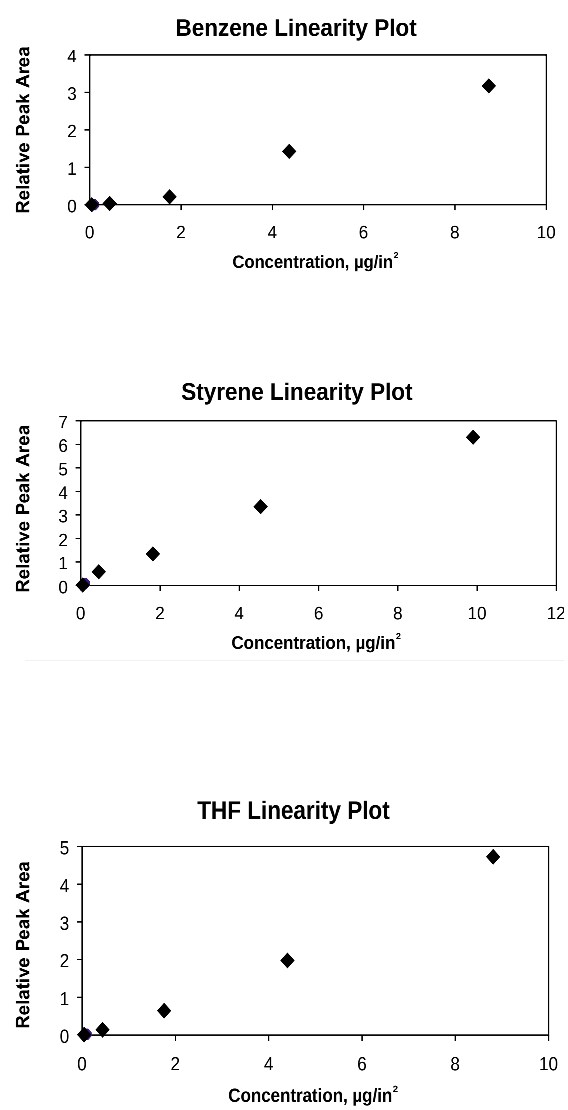
To develop a general method for monitoring volatiles in food contact packaging, we created a target list based on compounds that have been detected in processed packaging materials. The use of a mass spectral detector will enable the identification of other volatiles generated. We selected a low-bleed, Rtx®-5MS capillary column to allow analysis of the widest range of compounds. Initial separation parameters were entered into a computer modeling program, which optimizes the separation based on the column geometry, the oven temperature program, and the linear velocity (Table I, on the back page).

An internal standard (IS) solution of 4-butanone was prepared by diluting 300mL of 4-heptanone to 1 liter with purified water. The final concentration of the IS solution was 245mg/mL. The high standard solution was made by adding 50mL of each component to 475mL of the IS solution, and diluting to 500mL using the IS solution. Medium and low standard solutions were prepared using 25mL and 10mL of each component, respectively, and diluting each to 500mL using the IS solution. The chromatogram of a 12-component high standard solution is shown in Figure 1. Blank runs were performed before each standard and sample by analyzing a 100mL aliquot of the IS solution.

In order to determine the linearity of three packaging volatiles using this procedure, a series of standard solutions containing THF, benzene, styrene, and 4-heptanone (IS) were prepared and analyzed under the optimized parameters given in Table I. The standard preparation procedure described above also was used to prepare the linearity solutions. The approximate concentration range for each compound was 0-10µg/in². The linearity plots for three of the components are shown in Figure 2, with the relative peak area (peak area for the volatile/peak area for the IS) plotted vs. the concentration in µg/in². To further increase the sensitivity of this analysis, the MS can be operated in selected ion mode.

Figure 2

The Rtx®-5MS column exhibits good linearity for 3 volatile compounds that may be present in food packaging.



Tested over an approximate concentration range of 0–10 µg/in² for each component. R^2 = 0.992 (THF), 0.985 (benzene), and 0.994 (styrene).

Case Study of a Microwavable Bowl

A single-serving microwavable bowl was analyzed using the protocol outlined in the experimental conditions. The goal was to determine which volatiles the packaging material generates during microwave heating of this product. Testing was performed by sampling each of the discrete materials used in the package. In this study, this resulted in four samples: an inner bowl that contains the food; a plastic lid; a printed shrink-wrapped label sampled both at the seam and away from the seam. The materials were sampled by cutting a 10mm by 65mm piece into thin strips. Each sample was placed in a Tekmar purge and trap tube, along with 100mL of IS solution. Blanks (i.e., 100mL of IS solution) were analyzed prior to each sample. The samples were preheated to 60°C and held at this temperature for 10 minutes during purging. This temperature was selected based on the approximate temperature experienced by the packaging material when heated according to label directions.

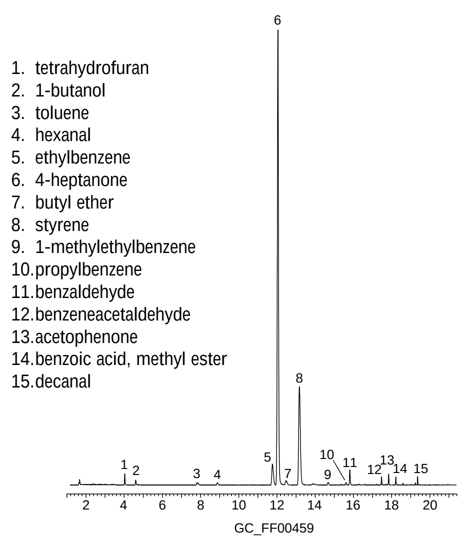
Based on this study, the highest level of volatile compounds was observed at the label seam. Residual styrene, ethyl benzene, and trace levels of solvents such as THF and toluene were detected. The label sampled away from the seam showed much lower levels of all of these components, except the styrene. The lid sample showed trace levels of ethylbenzene and styrene, while the inner bowl sample showed no significant levels of any volatile compounds. This procedure has proven to be an effective way to screen packaging materials for the presence of volatile compounds (Figure 3).

Figure 3

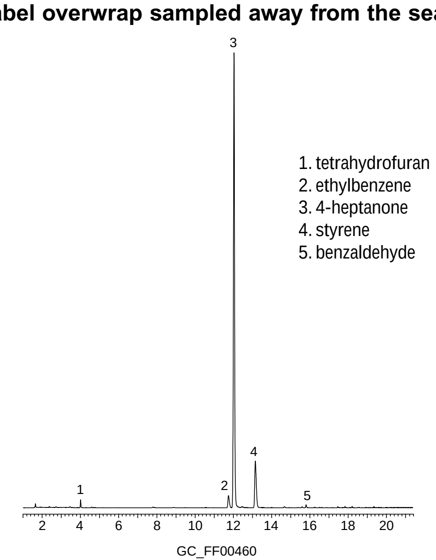
Screening microwave bowl materials for volatile compounds can be accomplished using the Rtx®-5MS column and the method outlined here.

See Table I, back page, for analysis conditions.

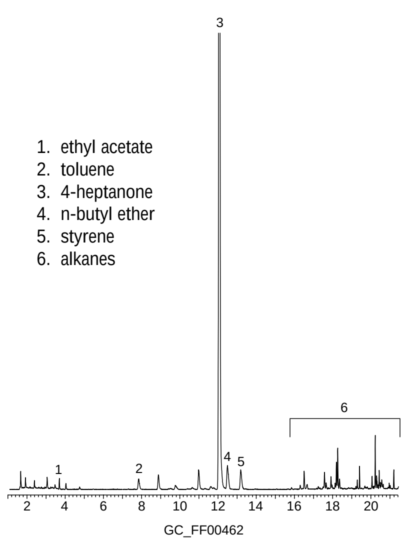
Label overwrap sampled at the seam



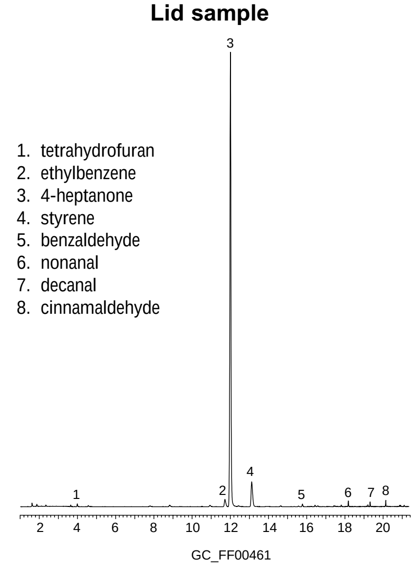
Label overwrap sampled away from the seam



Inner bowl sample



Lid sample



Conclusion

The analysis of food contact packaging is an important part of any food safety program. This is especially true with the wide variety of packaging materials available, the large range of intended use conditions, and the increasing popularity of convenience foods. With a continuing consumer emphasis on "speed to mouth," foods often are heated within the packaging material. This application note discusses an optimized procedure for monitoring common volatiles from food contact packaging using purge and trap GC/MS and an Rtx®-5MS capillary column. The Rtx®-5MS column is an excellent choice for this application. With its high stability and low bleed profile, it can be used to screen for a wide range of compounds by GC/MS. Please refer to the FDA to obtain more information on the regulatory requirements.

Table I

Optimized conditions and a low-bleed Rtx®-5MS column allow the analysis of a wide range of volatile compounds.

GC Parameters

Column: Rtx®-5MS, 30m x 0.25mm x 1.0µm (cat.# 12653)
Inj.: 250°C, 20:1 split
Carrier gas: helium, 1mL/min., constant flow
Oven: 50°C to 92°C @ 3°C/min, to 220°C @ 20°C/min. (1 min. hold)

MSD Parameters

Temp.: 280°C
Scan range: 35-260, 1 min. solvent delay
Ionization: EI @ 70eV

Purge & Trap Parameters

Concentrator: Tekmar LSC-3100 with Vocarb® 3000 (type K) trap
Transfer line: Silcosteel®-treated stainless steel tubing
Purge: 10 min. at 40mL/min., 60°C
Dry purge: 3 min. at 40mL/min.
Desorb: 2 min. at 40mL/min., 245°C

References

1. Schofield, J. Food FIPP Mag. (1989), 11(1), pp. 38-41.
2. Requirements of Laws and Regulations Enforced by the US FDA (1997), available on the US FDA website.
3. Marsili, Ray. "Techniques for Evaluating Packaging Materials" in Food Product Design (1997), editorial archives.
4. Annual Book of ASTM Standards (1998), American Society for Testing and Materials, West Conshohocken, PA.

References not available from Restek.

Product Listing

Rtx®-5MS Fused Silica Capillary Columns

ID (mm)	df µm	temp. limits	15-Meter	30-Meter	60-Meter
0.25	0.10	-60 to 330/350°C	12605	12608	12611
	0.25	-60 to 330/350°C	12620	12623	12626
	0.50	-60 to 330/350°C	12635	12638	12641
	1.00	-60 to 325/350°C	12650	12653	
0.32	0.10	-60 to 330/350°C	12606	12609	12612
	0.25	-60 to 330/350°C	12621	12624	12627
	0.50	-60 to 330/350°C	12636	12639	12642
	1.00	-60 to 325/350°C	12651	12654	
0.53	0.50	-60 to 320/340°C	12637	12640	
	1.00	-60 to 320/340°C	12652	12655	
	1.50	-60 to 310/330°C	12667	12670	

Purge-and-Trap Spargers

5mL Fritted Sparger, 1/2-inch mount: cat.# 21150
25mL Fritted Sparger, 1/2-inch mount: cat.# 21151

Moisture Control By-Pass Line

Moisture control by-pass line for Tekmar 3000: cat.# 21035

Restek Trademarks: MXT, Silcosteel, Rtx, and the Restek logo.
Other Trademarks: Vocarb (Supelco).