Odors and taints from paperboard food packaging

Philip A. Tice and Christopher P. Offen

ABSTRACT: Odorous substances, which can be present in paper and board food packaging and can cause tainting of the packaged food product, are identified and the various sources listed. Quality assurance tests to monitor packaging for unacceptable odors and a propensity to taint foods are discussed, together with analytical procedures for identifying the chemical nature of odorous and tainting substances.

KEYWORDS: Chemical analysis, food boards, odors, organoleptic tests, packaging papers, procedures, quality control, taste, test methods.

To meet consumer demands for improved food quality and market requirements of longer shelf-life, today's packaging has become quite sophisticated.

Taste and aroma are some of the more important qualities of foods, and these organoleptic properties are protected by the packaging, which performs the dual role of retaining the flavors and aromas of the foods and preventing external contamination by undesirable substances. However, care must be taken in the selection and quality of the packaging to ensure that the packaging itself is not a source of substances that can adversely affect the organoleptic properties.

Paper and cartonboard have been used both as primary and secondary packaging to package a wide range of foods for many years. Today, paper and cartonboard materials often are incorporated with adhesives, varnishes, and plastics as part of a multilayer structure. All these components can contain substances that could be responsible for odors and food tainting.

Plastics and board composites are used commonly for packaging beverages and other liquid based foods. Although the plastics layer provides an effective barrier to the liquid contents, volatile substances have been known to permeate from the board to the beverage or foodstuff.

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Testing paperboard packaging for odors and propensity to taint foods

Producers and users of food packaging carry out regular taint and odor tests as part of their quality assurance programs. These tests determine whether or not the packaging has an unacceptable level of odor or a propensity to taint the packaged foods, or both. For paper and cartonboard food packaging, the Robinson test has become the standard for many European companies in recent years.

Since the laws of the European Community and the Member States specify that food packaging should not adversely affect the organoleptic properties of the packaged foods, methods of organoleptic testing based on the Robinson test currently are being drafted for a European Standard by Technical Committee 172 of the European Committee for Standardization.

Taint and odor test methods used in the United Kingdom for almost 30 years are contained in British Standard BS 3755, which was originally introduced in 1964 and revised in 1971.

With papers and cartonboards the liberation of odors and potential for food tainting are influenced by the level of moisture in the material. Therefore, organoleptic tests are prescribed with water added to the sample containers to generate a humid atmosphere and increase the level of moisture in the test samples.

The German DIN Standard 10 955 contains taint tests for primary and secondary packaging where the food is either in direct contact with the packaging or where tainting can arise due to vapor transfer.

In the United States, the American Society for Testing and Materials (ASTM) Standard E 619-84 contains a procedure for the assessment of odors in paper packaging and for corresponding taint tests.

All these standards are based on similar procedures. For odor testing, specimens of the paper or cartonboard sample are placed in containers that are sealed and stored for a specified period at ambient temperature. The containers are opened, and a trained panel assesses whether there is an odor. Where an odor is detected it is rated on intensity.

With taint tests, the packaging is exposed to a test food in sealed containers, either by direct contact or by vapor transfer, for a specified period at ambient temperature. A similar quantity of the test food is stored in another sealed container to act as the "control" food. Then a trained panel is asked to determine whether there is a difference in taste between samples of the food that have been exposed to the packaging and "control" food. The assessments are now usually performed by means of the "triangle test," where each panel member is given three samples of food to taste—one which has been exposed to the packaging and two "controls"—and asked to say which has a different taste. The results from the panel are analyzed statistically to account for any "correct" answers arrived at by chance.

Odorous volatiles causing tainting in packaged foods

The transfer of odorous substances from packaging to food may not necessarily involve any direct contact between the packaging and the contained food. Odorous volatiles released from the packaging material into the vapor phase within the package can be absorbed by the surface layer of the food and slowly diffuse into the interior. The absorption of the volatiles by the food causes a change in the equilibrium between the molecules in the solid and vapor states and leads to further evaporation of the odorous substances to the vapor state and to their transfer to the food. Most odorous substances absorbed by the packaged food will cause tainting, but the tainting threshold levels can be quite different for different foods.

Where there is direct contact between the packaging and the food, transfer of odorous and tainting substances is more likely to occur if there is penetration into the packaging of components of the food, such as oils and fats. This is a well recognized migration mechanism.

Unacceptable odors in packaging need not be unpleasant odors. Very much like the classical definition of a garden weed, it can be a case of "something being present in the wrong place at the wrong time." For example, octenol, which is sometimes present in board materials, has a characteristic "fungal" smell and although this may be acceptable in the packaging of food products such as mushrooms, the consumer would find it unacceptable with products like chocolates. Phenols and cresols contribute to the characteristic aroma and taste of Scotch whisky but would be regarded as unacceptable taints if found in dairy products.

The sources and mechanisms of formation of substances from packaging materials responsible for organoleptic contamination are complex and can arise from:

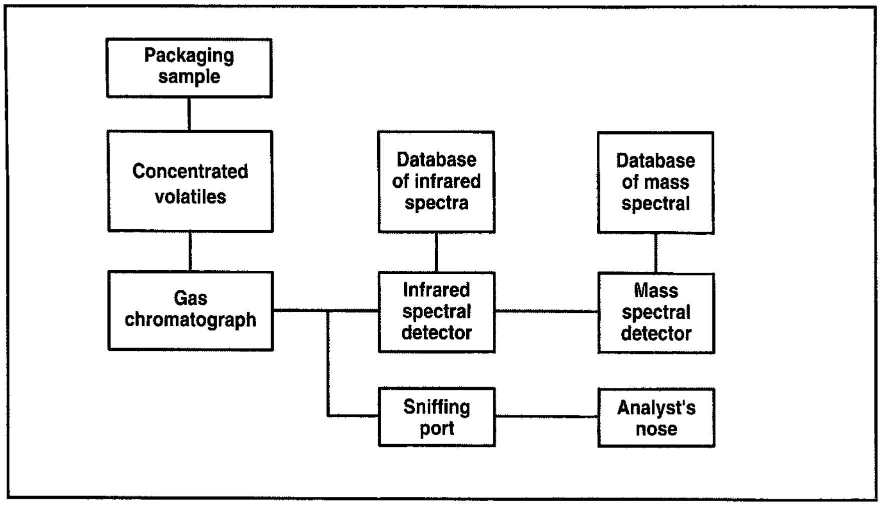
- **Inappropriate raw materials, contaminants in raw materials, and unintentional contamination during the manufacturing of the packaging material.** Incorrect manufacturing conditions also can generate undesirable organoleptic substances. Such sources of taint and odor generally indicate inadequate quality assurance of the raw materials and inadequate quality control of the manufacturing process.
- **Substances from chemical reactions that occur within the packaging material and which sometimes continue after the material has been produced and finished.** The levels of these substances can consequently increase with storage time of the packaged food. This mechanism of formation of odorous substances has been found to occur with some paper and cartonboard packaging materials.
- **Abnormal storage and transport conditions**, such as high temperatures and humidity, causing microbial activity.
- **Volatile substances present from printing or coatings used on the packaging material, particularly solvent residues.** Printing is nearly always on the outside of the packaging, but contamination of the packaged food by print volatiles can result from reverse-side contact of the packaging before use; that is, when the printed surface comes into contact with the food surface or when the print volatiles permeate through the packaging matrix to the food. With secondary packaging, contamination can occur by vapor transfer.

Chemical identification of tainting and odorous substances

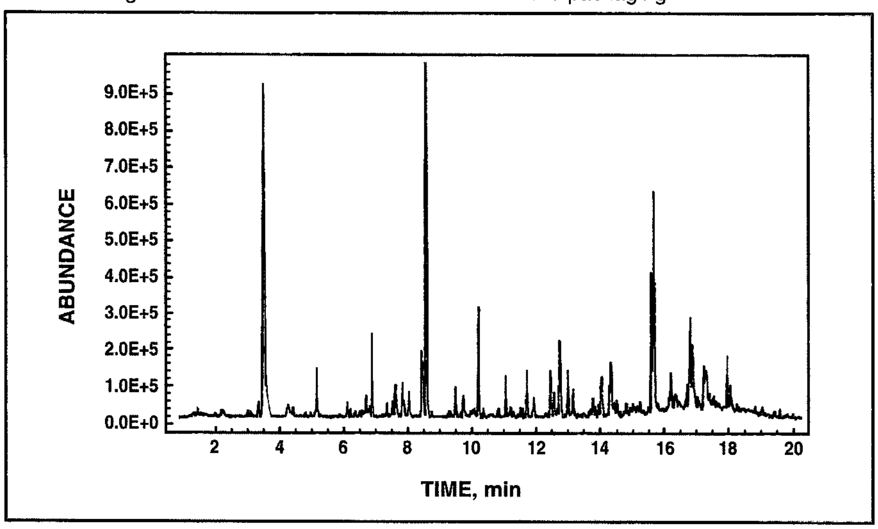
The taint and odor tests previously described simply determine whether or not the packaging has a detectable odor and whether or not it has a propensity to taint packaged food.

If the tests reveal that there is a detectable odor at a level and nature considered unacceptable, or that the packaging is likely to taint the food,

1. Analytical system for the isolation and analysis of odorous volatiles from packaging material



2. Chromatogram of volatile substances from cartonboard packaging



it is necessary to identify the offending substance or substances and their source. This information is essential to creating packaging with an acceptable level of quality.

The various possible sources of odorous and tainting substances from components of packaging materials have been described, and a trial and error approach to eliminate offending odorous and tainting substances could be very time consuming and costly.

The analytical identification work usually starts with odorous substances since, when present at appropriate concentrations, these usually are responsible for any food tainting. There can be, however, occasions when food tainting occurs and the substance responsible did not have an easily detectable odor.

Odorous volatiles and tainting substances may be isolated from packaging material by conventional methods of solvent extraction or by trapping and concentration onto polymeric absorbent materials. Chemical identification is based on modern analytical chromatographic and spectroscopic systems such as GC-MS/IR. Gas chromatography (GC) is used to resolve and separate individual components from within a mixture of volatiles, which are then detected and identified by mass spectral (MS) and infrared (IR) spectral analyzers. The MS and IR detector systems provide complementary information to aid identification.

Each isolated chemical substance produces characteristic "fingerprint" MS and IR spectra, which are matched for identification against thousands of library spectra in online databases.

Also, the analytical system usually is equipped with an olfactory or "sniffing" port, which enables odors from the separated components to be monitored by the analyst's nose.

The mass spectral detector has the advantage that, when operated in the selective ion monitoring mode (SIM), extremely low levels of substances can be detected and analyzed. The analytical system is shown in **Fig. 1**.

In **Fig. 2**, a chromatogram is displayed from an analytical investigation for odorous volatiles from cartonboard packaging. The chromatogram had been obtained using the analytical equipment described above and shown in Fig. 1.

The large chromatogram peak at 3.1 minutes occurred at the same time as a strong odor was detected at the "sniffing port." The infrared spectrum of the substance responsible for the peak was obtained and from a search of the library database the best match was for the aldehyde hexanal. A search for the best match also was made for the corresponding mass spectrum, and this too was found to be for the aldehyde hexanal. The infrared and mass spectra and the reference spectra from the libraries are shown in **Figs. 3 and 4**.

Hexanal is commonly found in paper and cartonboard at low levels and has an odor that is usually described as "grassy." At low levels the odor from hexanal is not unpleasant and, being associated with the natural origins of the product, is accepted by users and consumers.

Sources of odorous substance in paper and board food packaging

Although plastics are now the most widely used food packaging material, paper and board still find many applications. Odorous substances can arise from a number of sources and many of these apply to paper and board packaging.

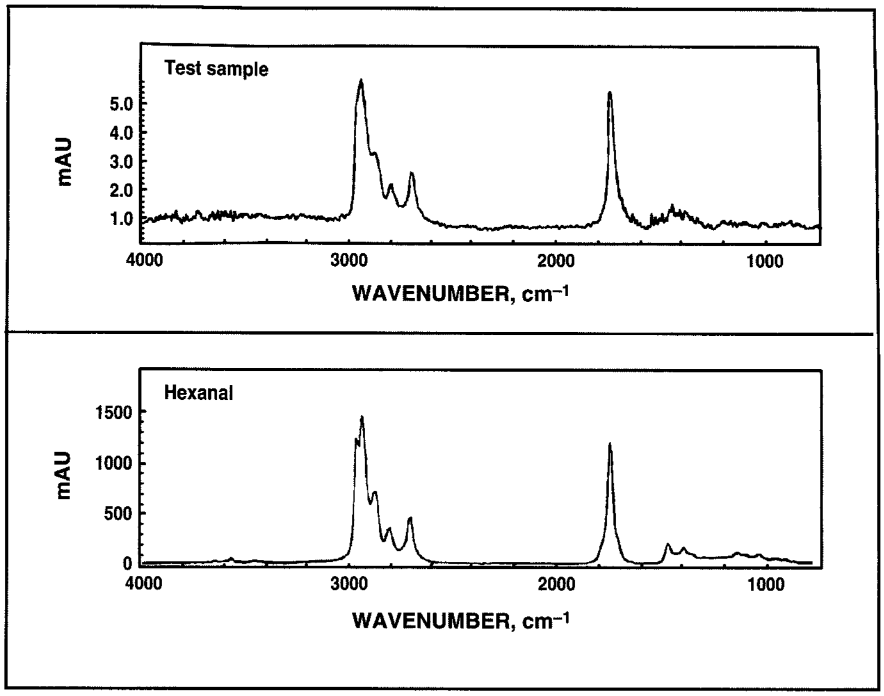
Some cartonboard consists of more than one layer and also may have surface coatings for printing and appearance. These usually consist of a filler and a synthetic resin binder, such as styrene–butadiene or styrene–acrylate copolymers.

Where styrene–butadiene-type binders have been used, a number of volatile substances present as by-products from the polymerization process have been identified. Volatiles detected included styrene monomer and vinyl cyclohexene, together with a number of alkyl substituted benzene compounds. Of these, 4-phenyl cyclohexene has been found to have a particularly strong "synthetic latex" odor. All these substances have distinct and characteristic odors and if present in sufficient quantities can make the board unacceptable for packaging foods.

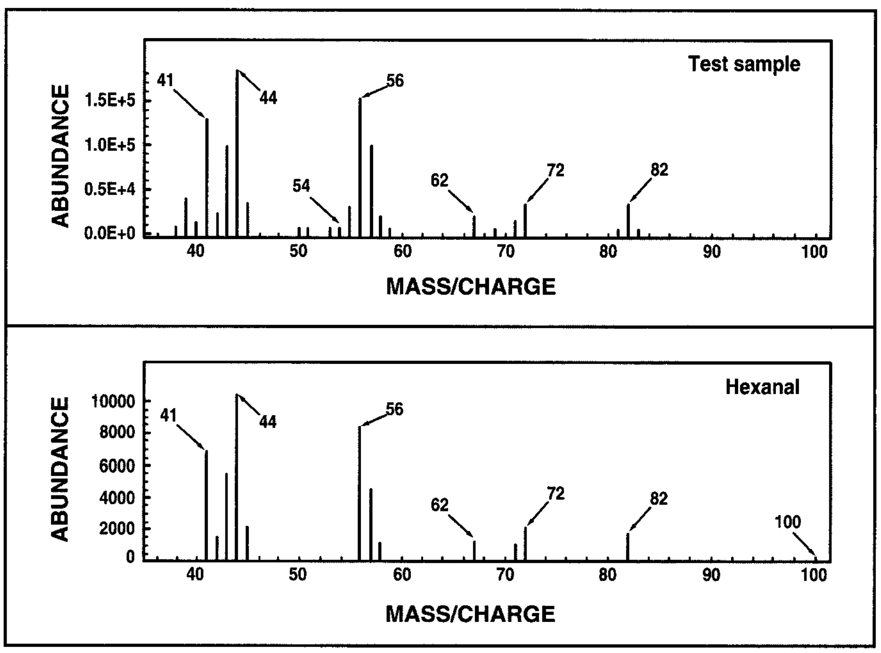
Odorous substances that may be present in paper and board materials can originate by a variety of mechanisms, such as actions of bacteria and molds, autooxidations of residual wood resins, and degradation of processing chemicals *(1)*. Also, metallic ions such as those of iron and copper, present in inorganic residues from the pulp, can catalyze the oxidation of lipids and other components originating from resinous fractions to a range of odorous volatiles.

These odorous volatiles are typically substances containing functional groups such as aldehydes, alcohols, esters, sulfides, and also those with unsaturated groups. Usually most of these substances are present at very low levels, and their odors are barely detectable.

3. Infrared spectrum of peak in chromatogram at 3.1 minutes and reference library match for hexanal



4. Mass spectrum of peak in chromatogram at 3.1 minutes and reference library match for hexanal



Some paper and board volatile substances have odors that are not unpleasant and at low levels can be easily tolerated, such as the aldehyde hexanal previously mentioned.

On occasion, food packaged in cartonboard has become tainted due to contamination by chlorophenols and chloroanisoles. Chlorophenols can be formed as by-products of chlorine bleaching of wood pulp. Timber used for pulp manufacture has on occasion been treated with pentachlorophenol to prevent fungal decay. This particular chlorophenol also has been used as a biocide in aqueous-based adhesives for glued seams of paper sacks and cartons used for bulk packaging of cocoa, tea, and dried fruits.

In a number of reported incidents of tainting of packaged foods by chlorophenols, the contamination of the packaging has been traced to wood pallets on which the cartons had been transported or stored. Pentachlorophenol has been a commonly used biocide for treatment of pallet wood.

The chlorophenols are highly odorous and have extremely low taint threshold values in many foods and beverages, consequently tainting is caused when only "trace" contamination occurs. The taints are usually described by the layman as "disinfectant" or "medicinal."

The chloroanisoles are methylated derivatives of chlorophenols and have been shown to be formed by microbial action on chlorophenols *(2)*. Therefore, the chloroanisoles often are found together with chlorophenols, particularly where adequate moisture is present in products such as wood and cartonboard to promote microbial activity.

Whereas the chlorophenols are highly odorous and can readily taint foods, the chloroanisoles must be described as very highly odorous, with the ability to taint foods easily at the subparts per billion level. The chloroanisole odors are "musty," and the taints have a similar character.

Unlike many other packaging materials, which after manufacture can become less odorous, some paper and board materials have been found to become more odorous during storage, both before and after packaging of the food. This has been attributed to on-going oxidation reactions, probably catalyzed by metal ion residues, resulting in the liberation of chemical substances such as aliphatic aldehydes. Complexing agents often are added to the pulp during manufacture to reduce the catalytic action of the metal ion residues, thus minimizing the formation of the odorous substances. In addition to the aliphatic aldehydes, heterocyclic aldehydes such as furfural also have been identified in paperboard materials.

Printing inks and varnishes

Although printing inks and varnishes are applied to the exterior of packaging, they can represent a potential source for odors and tainting in packaged foods. Most forms of printing use inks consisting of pigments and resins dissolved or dispersed in a solvent, traditionally of an organic type. Unless there is a functional barrier in the packaging material, components of the print and varnish, such as solvent residues, can permeate through the packaging and migrate into the packaged food. Normally these levels are extremely low and do not result in detectable odors or tainting of the food.

To ensure that printed paper and board packaging has the required organoleptic qualities, it is advisable to take care in selecting inks and varnishes and to maintain good control over the printing and drying processes.

With litho inks the principal solvents used are petroleum distillates. For printing food packaging these solvents are selected to have low levels of odorous aromatic hydrocarbons. Resins used in litho inks also can present a potential source of odorous substances. These resins are normally alkyds, which oxidize in the drying process and can liberate odorous by-products such as aldehydes and ketones.

Flexographic inks use a variety of solvents, but for food packaging they are mainly based on alcohols (ethanol, propyl alcohol) and esters (ethyl acetate, propyl acetate). With flexographic printing these solvents represent the most likely source for unacceptable odors, in particular the acetate esters. Therefore, it is essential that any solvent residues be reduced to a low level at the drying stage. Toluene and xylene, which are odorous aromatic hydrocarbons, have been used in the past but are now rarely used for food packaging. Flexographic ink resins include polyamides, cellulose nitrate, and acrylics. It is very unusual for these to cause either an odor or taint problem.

Solvents and resins used in gravure inks and varnishes for food packaging are similar to those used for flexographic printing inks.

Today food packaging is often printed with water-based inks and varnishes because of their low odor and taint properties. A proportion of alcohol solvent usually is incorporated in the ink formulations.

Ultraviolet-cured inks and varnishes are basically solventless, consisting of acrylate monomers with a photoinitiator such as benzophenone. Some acrylate monomers can have highly characteristic odors. However, acrylate formulations now in use have very low odors and, although they can give a characteristic "acrylate-type" odor straight off the press, this usually dissipates quickly. Any trace odors from this form of printing and varnishing probably are due to a combination of minor acrylate residues, benzophenone or other photoinitiators, and reaction by-products from the polymerization process.

The potential for components of printing on paper and board packaging to cause objectionable odors has been recognized for a long time, and research studies have been carried out to investigate the problems. The type of pulp involved in the board manufacture has been found to have a significant influence on levels of residual printing solvents that may be retained in the material and lead to unacceptable odors. Boards made from a proportion of mechanical pulp have been shown to absorb and retain residual solvents to a higher degree than those made only with chemical pulp. Similarly, other board components such as pigments and coatings have different abilities to retain residual solvents *(3)*.

If printing is carried out correctly the levels of volatiles with the potential to cause taint and odor are minimized. However, there have been cases where levels of print solvents have reached unacceptable concentrations resulting in odor and tainting problems.

There are a number of standard methods for measuring the levels of retained solvents in printed packaging. In the United Kingdom, BS 6555 contains methods for monitoring the levels of residual solvents in flexible packaging materials. In the United States, the ASTM method for the determination of residual solvents in flexible barrier materials is described in F-151-86. Both these test methods are applicable to printed paper and board food packaging.

An interesting example of an off-odor resulting indirectly from printing solvents is that of 4-methyl-4-mercaptopentan-2-1, a hydrogen sulfide adduct of mesityl oxide. This odor, best described as "catty," has been found to be associated with meats and other foods containing sulfur compounds *(4)*. In an extensive investigation to trace the source of this odor in a "cook in the bag" ham product, mesityl oxide was demonstrated to have originated from diacetone alcohol present as a solvent residue in red printing *(5)*. The formation of the mesityl oxide is thought to have arisen from dehydration of the diacetone alcohol and promoted by a "property" of the ionomer layer in the bag material. Mesityl oxide also can be formed from acetone, a solvent used on occasion in coatings and adhesives.

Conclusions

Quality assurance testing of paper and board food packaging materials usually ensures that the products supplied to the food packer are free from unacceptable odors and any potential for tainting the packaged foods.

Paper and board materials, however, can contain a wide variety of substances that have the potential to adversely affect the organoleptic properties of packaged foods. When on rare occasions one or more of these substances reaches organoleptically detectable levels in the packaged foods a problem exists. To solve the problem and return the packaging to its normal quality standard, it is essential to identify the chemical nature and source of the "offending substances." Since the "offending substances" are usually present at very low levels, the analytical investigation requires sensitive analytical instrumentation and an analyst with the necessary experience and expertise.

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