Organohalogen Taints in Foods
Foreword

Every year the food industry receives complaints from consumers concerning off-flavours and taints in fresh, processed and packaged foods. Fortunately, many of these are only isolated cases, although on occasions major problems are encountered which may involve, for example, the recall and destruction of several days’ production or the condemnation of several freight container loads of packaged foods.

For many years, the food industry worldwide has been confronted with severe tainting of various foods due to the presence of halogenated phenols (or halophenols) and their related anisoles (together referred to as organohalogens) originating mainly, but not exclusively, from the chemical treatment of wooden pallets and container floors. Such taints continue to be a major source of concern to the food industry, and of annoyance to consumers.

While there are seldom health concerns arising from taints, the tainting is very objectionable and the threshold levels are extraordinarily low. The mechanism of tainting has been studied since the 1960’s and the scientific literature is considerable. Over the past 30 years, the Australian food industry has experienced (and continues to experience) many tainting cases resulting in serious losses.

The goal of this booklet is to avoid these losses, or at the very least reduce them to an acceptable level, through increasing awareness about the sources of organohalogen taints and their prevention. It is apparent that many of those working in the Australian food industry today are unaware of the detailed scientific work undertaken in Australia and elsewhere over the past 30 years in connection with the organohalogen tainting of foods. As George Santayana said “Those who cannot remember the past are condemned to repeat it”. It is hoped that through the publication of this booklet, information about the cause and prevention of organohalogen taints will be more widely known throughout the food industry.

This booklet has been prepared by a working group of the Scientific and Technical committee of the AFGC; it will be widely distributed to all those in the food supply chain. The AFGC is grateful to those members who freely gave of their time to contribute to the preparation of this booklet and shared their own experiences of organohalogen taints.

Dick Wells
Chief Executive
Australian Food & Grocery Council
Canberra

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Introduction and definition

A taint is a taste or odour totally alien to the food and normally arising from external sources, in contrast to an off-flavour or off-odour which is an atypical taste usually associated with internal deteriorative changes to components in the food. All taints are contaminants, but not all contaminants are taints.

The odour or taste threshold of a taint is defined as the lowest concentration of a compound detectable by a certain proportion (usually 50%) of a given group of people, although note that not all the reported threshold values for organohalogens have been determined this way. The threshold is not an inherent property of the chemical because the threshold for any substance will vary with the medium in which it is present (ie the food or drink) and between different people (Land 1989). For example, the threshold values for chloroanisoles increased in the order water, dried fruit, fruit buns and plain buns, the increase being attributed to the relative amount of lipid present (Whitfield & others 1987). Although a taint could only rarely be detected by smell in the dried fruit itself, it was easily recognised by consumers when the baked products were eaten.

The wide range of human thresholds to chemical stimuli is a major reason for the difficulties in preventing food taints and in positively identifying the causes of taints. The threshold concentration difference between the most sensitive 5% and the least sensitive 5% is nearly 2000-fold. This clearly demonstrates why most complaints about taint arise from only a small proportion of those purchasing a particular batch of tainted product since in most cases only the more sensitive detect it as a taint.

This large range of sensitivity between individuals explains many of the inconsistencies in the reactions of different people to the same sample, and the apparent sporadic appearance of taints. This can make detection difficult, although it may also limit the impact of the problem. It is therefore prudent to take action on the basis of a warning by only one panellist of known high sensitivity (Kilcast 1996). Because chloroanisoles (and probably bromoanisoles) are known to cause powerful fatigue/adaptation effects, exposure to one sample can prejudice the perception of subsequent samples. This precludes asking panellists to assess more than one sample per testing session (Whitfield & others 1987).

Organohalogen Taints in Foods

Organohalogens

The major organohalogens (organic compounds containing chlorine, bromine or iodine) of interest to the food industry are the halophenols and haloanisoles, the structure of two of the most common being shown in Figure 1.

![Figure 1. Structure of two of the most common organohalogen compounds.](image)

Halophenols

Halophenols are important industrial compounds used as chemical intermediates or as finished products. There are 19 congeners of chlorophenols, from the mono-chloro to the well-known pentachlorophenol (PCP) that has been widely used as a fungicide (“anti-blue agent”) for wood protection. Tribromophenols (TBP) and their derivatives have been recommended as fire-retardant agents as well as wood preservatives and general fungicides for use with leather, textiles, paint, plastics, paper and pulp. A survey into the occurrence of bromophenols in Australia (Whitfield & others 1997) found that some samples of corrugated fibreboard, manufactured from imported medium and linerboard, were contaminated with high concentrations of TBP.

Numerous cases of contamination have been reported in the literature with “disinfectant” or “medicinal” descriptors. The problem is generally traced back to the presence of halophenols in very small amounts. These compounds have low sensory thresholds and can impart taints to foods at concentrations in the ppb (parts per billion) or ppt (parts per trillion) range.

The following analogies may help in understanding the magnitude of such low concentrations:

- one ppt is equal to one grain of wheat in 100 000 tonnes. 100 trains each with 25 wagons are needed to transport 100 000 tonnes of wheat.
- one ppt is equal to 0.4 mm (the thickness of a credit card) of the total distance from the Earth to the Moon.
- one ppt is equivalent to 1 second in 31 797 years.
Haloanisoles

Chloro- and bromoanisoles are produced by fungal methylation of the parent halophenols under humid and warm conditions (xerophilic fungi require a moisture content between 12 and 16% and a temperature between 25 and 35°C for germination and growth). They impart “musty” and “mouldy” taints to foods at extremely low concentrations (see Table 1). Haloanisoles are also responsible for the well-known “cork taint” in wine (Sefton & Simpson 2005) and the “Rio flavour” in coffee (Spadone & others 1990, Czery & Grosch 2000).

Sensory characteristics

Because consumers complain more often about the flavour rather than the odour of ‘musty’ foods, flavour or taste (ie in the mouth) thresholds are a more valid indicator of the tainting importance of organohalogens. Sensory characteristics of selected organohalogens and their thresholds are shown in Table 1.

<table>
<thead>
<tr>
<th>Organohalogen</th>
<th>Olfactory sensation</th>
<th>Odour threshold µg/L (ppb)</th>
<th>Taste threshold µg/L (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-CP</td>
<td>Iodine/medicinal</td>
<td>0.36&lt;sup&gt;a&lt;/sup&gt;, 2&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.1&lt;sup&gt;a&lt;/sup&gt;, 0.14&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>4-CP</td>
<td>Iodine/medicinal</td>
<td>20&lt;sup&gt;a&lt;/sup&gt;, 60&lt;sup&gt;b&lt;/sup&gt;</td>
<td>39&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>2,4-DCP</td>
<td>Iodine/medicinal</td>
<td>0.4&lt;sup&gt;a&lt;/sup&gt;, 29&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.3&lt;sup&gt;a&lt;/sup&gt;, 0.98&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>2,6-DCP</td>
<td>Iodine/medicinal</td>
<td>3.5&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.0062&lt;sup&gt;a&lt;/sup&gt;, 0.2&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>2,4,6-TCP</td>
<td>Iodine/medicinal</td>
<td>300&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2&lt;sup&gt;a&lt;/sup&gt;, &gt;12&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>2,4,6-TCA</td>
<td>Earthy/musty</td>
<td>9 x 10&lt;sup&gt;-5&lt;/sup&gt;&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.02&lt;sup&gt;d&lt;/sup&gt;, 0.025&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>2-BP</td>
<td>Phenolic, iodine</td>
<td>0.1&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.03&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>4-BP</td>
<td>Phenolic</td>
<td>4&lt;sup&gt;b&lt;/sup&gt;</td>
<td>23&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>2,4-DBP</td>
<td>Iodoform</td>
<td>0.5&lt;sup&gt;b&lt;/sup&gt;</td>
<td>4&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>2,6-DBP</td>
<td>Phenolic</td>
<td>0.1&lt;sup&gt;b&lt;/sup&gt;</td>
<td>5 x 10&lt;sup&gt;-4c&lt;/sup&gt;</td>
</tr>
<tr>
<td>2,4,6-TBP</td>
<td>Iodoform</td>
<td>0.1&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.6&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>2,4,6-TBA</td>
<td>Earthy/musty</td>
<td>2 x 10&lt;sup&gt;-5d&lt;/sup&gt;</td>
<td>ND</td>
</tr>
<tr>
<td>PCP</td>
<td>Phenolic</td>
<td>23&lt;sup&gt;a&lt;/sup&gt;, 1600&lt;sup&gt;e&lt;/sup&gt;</td>
<td>8&lt;sup&gt;a&lt;/sup&gt;, 30&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>Phenol</td>
<td>Phenolic</td>
<td>31&lt;sup&gt;a&lt;/sup&gt;, 4000&lt;sup&gt;e&lt;/sup&gt;</td>
<td>&lt;2&lt;sup&gt;a&lt;/sup&gt;, 300&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

2-CP: 2-Chlorophenol 4-CP: 4-Chlorophenol 2,4-DCP: 2,4-Dichlorophenol 2,6-DCP: 2,6-Dichlorophenol 2,4,6-TCPC: 2,4,6-Trichlorophenol 2,4,6-TCA: 2,4,6-Trichloroanisole 2-BP: 2-Bromophenol 4-BP: 4-Bromophenol 2,4-BBP: 2,4-Dibromophenol 2,6-BBP: 2,6-Dibromophenol 2,4,6-BBP: 2,4,6-Tribromophenol 2,4,6-TBA: 2,4,6-Tribromoanisole PCP: Pentachlorophenol ND: not determined.

History and sources of taints

Of the nearly 3200 known naturally occurring organohalogen compounds, more than 1600 contain bromine. Organobromines are produced by marine and terrestrial plants, marine animals, bacteria, fungi, some higher animals and a few mammals including humans. For example, methyl bromide (bromomethane) is produced in significant quantities from natural soil bromide by plants such as rapeseed, mustard, cabbage, broccoli, turnip and radish, this source of natural methyl bromide contributing significantly to the overall atmospheric concentration of methyl bromide (Gribble 1999).

In the early 1960s, TNO investigators in the Netherlands identified chloroanisoles as the cause of a musty taint in eggs and broilers, the source of the taint being the cage litter which contained wood shavings that had been treated with chlorophenols (Engel & others 1966); similar taints were identified in England in the 1970s (Land & others 1975). At the time of these incidents, most soft wood was treated with pentachlorophenol (PCP) (which also contained significant quantities of tetrachlorophenol (TeCP) and trichlorophenol) to prevent the formation of fungi which impart a blue/purple stain (sapstain) to the wood. Today the use of PCP has been discontinued in most countries.

In the early 1980s, the presence of polybrominated anisoles and organochlorine compounds in marine fauna and sediments in Japan was reported (Miyazaki & others 1981, Watanabe & others 1983). 2,4,6-TBA (tribromoanisole) was found in several samples with a maximum level of 5.4 ppb. Its presence was explained in two different ways: chlorination of water in the presence of bromine and the use of 2,4,6-TBP as a flame retardant, the TBP being transformed to TBA by microorganisms. 2,4,6-TBP is used as a flame retardant in epoxy resins, polyurethanes, plastics, paper, textiles and other products. It may also be used...
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as an intermediate for the production of other commercial flame retardants and fire extinguishing media, and can be used as an antiseptic agent. TBP is also readily formed from the chlorination of water containing phenol and bromide (Sweetman & Simons 1980). Bromophenols generally have lower sensory threshold values than chlorophenols and therefore have much higher tainting potential (Adams & others 1999).

Australian research

Dr Frank Whitfield and his colleagues at the CSIRO Food Science laboratories in North Ryde, Sydney studied organohalogen compounds for over 30 years and published many papers on organohalogen taints in foods and packaging materials, as well as bromophenol off-flavours in marine organisms.

Organohalogens have been detected in a range of packaging materials in Australia. Cocoa powder imported in multiwall paper sacks was found to contain a number of chlorophenols and chloroanisoles. The paper sacking was considered the source of these compounds which were formed during the bleaching of wood pulp (Whitfield & others 1984). Many of the fungi isolated from fibreboard cartons, paper sacks and jute sacks used to package food were able to produce 2,4,6-TCA from 2,4,6-TCP (Tindale & others 1989).

Chlorophenol formation by action of chlorine-based sprays on phenols naturally present in fibreboard cartons and wooden pallets from decomposition of lignin has also been reported (Tindale & Whitfield 1989). Microorganisms converted chlorophenols to chloroanisoles which gave a musty taint in dried fruit.

Shipping containers have been responsible for many food tainting incidents (Whitfield & others 1994). Analysis of the floors of 16 randomly selected shipping container floors for chlorophenols (Whitfield & others 1989) revealed that seven of the floors had concentrations of TCP and TeCP > 15 µg/kg (ppb). The chlorophenols could have originated from previous cargoes such as leather hides, or pre-treatment of the timber floor with a chemical preservative based on a xerophilic fungus Paecilomyces variotii can convert the fungicide 2,4,6-TBP to the musty-smelling metabolite 2,4,6-TBA in fibreboard cartons. Some samples of corrugated fibreboard in Australia manufactured from imported medium and linerboard were found to be contaminated with high concentrations of TBP. The TBA produced a musty taint in sultanas packaged in polyethylene pouches after only one week of storage in the presence of fibreboard containing TBA (Whitfield & others 1997).

A musty off-flavour in several brands of beer in Australia was traced to the absorption of TCA into the internal lacquer of aluminium cans during transportation from the can manufacturer to the brewery in shipping containers. The cans ends were similarly transported and TCA was preferentially absorbed by the solvent-based sealing compound of the can ends. Both the ends and the internal lacquer of the cans resulted in subsequent tainting of the canned beer (Lambert & others 1993). To prevent further incidences of TCA contamination of beer, the can manufacturer uses only one-way wooden pallets and top frames to stack empty beer cans; all shipping containers have a foil laminate liner; layer divider boards are of low moisture virgin kraft; and ends, pre-wrapped in paper sleeves, are transported on similar pallets lined with a foil laminate barrier material. Lambert & others (1993) recommended that can manufacturers worldwide should consider adopting similar specifications.
for transportation of aluminium cans, and noted that although these procedures increased the transportation cost, they remain essential if sporadic losses of large volumes of beer are to be avoided.

**Taints in wines**

Organohalogens are responsible for taints in wine, a musty or corked character in wines (referred to as cork taint) having long been associated with 2,4,6-TCA with 1–5% of corked wines being affected (Sefton & Simpson 2005 and references therein). Although TCA has been recognised since 1982 as the major cause of cork taint in bottled wine (Buser & others 1982), about 12 other compounds have been implicated although their role has not received adequate attention and is incompletely understood (Sefton & Simpson 2005). However, in a recent review (Pereira & others 2000), the authors concluded that faulty corks were responsible for only a minority of contaminated wines, and targeting TCA contamination of cork closures as the major cause of wine taint is not justified.

A recent survey of 2400 wines from northern hemisphere wineries found that many wines exhibiting cork taint had low or undetectable concentrations of 2,4,6-TCA (Soleas & others 2002). The authors concluded that TCP and TCA are, at most, minor components of cork taint in commercial wines. Their critical examination of the primary data on which the original assertions are based revealed small sample numbers, a tendency to ignore anomalous results, and the absence of any statistical proof for the asserted relationship. Their study has been criticised by Sefton & Simpson (2005) on the grounds that the analysis was conducted without an internal standard, had no means of ensuring peak homogeneity and was based on a standard addition curve with concentrations three orders of magnitude greater than those determined in real wine samples. They also criticised the fact that wine was categorised as tainted if assigned as such by as few as one of an unknown number of assessors.

An important form of cork taint described as ‘fungal must’ and considered to be second only to TCA in importance has recently been identified as 2-methoxy-3,5-dimethylpyrazine (Simpson & others 2004). It has an aroma threshold in white wine of 2.1 ppt and has also been identified in coffee where it was described as having an earthy aroma (Czerny & Grosch 2000). It was first reported as being responsible for an obnoxious odour (musty, foul drains or sour dishcloths) present in certain machine cutting emulsions used in engineering workshops (Mottram & others 1984). The origin of this compound in corks is unknown but, unlike TCA, it is not necessarily bacterial; the cutting punches that produce the cork cylinders could be one possible source (Simpson & others 2004). It is considered that it could be a cause of many instances of taints in the environment and in foods and beverages, but because of the difficulty in analysing for it and its exceedingly low threshold, it has not been identified as such. Other pyrazines including 2-methoxy-3-isopropylpyrazine have been identified in cocoa beans having a mouldy taint (Baigrie & others 1987).

Recently French researchers identified 2,4,6-TBA in wines, causing pungent, musty odours in the absence of chloroanisoles (Chatonnet & others 2004). The TBA came from the precursor TBP, and both derived mainly from environmental pollution in wineries where the atmosphere was contaminated with TBA coming from TBP used recently to treat wood or originating from much older structural elements of the winery or from used wooden containers. In certain cases, although the initial source had been eliminated, residual pollution adsorbed on walls or found in old barrels could be sufficient to make a building unsuitable for storing wines or sensitive materials (including corks and glass bottles) intended for direct contact with wine. When wine is tainted prior to bottling, the taint is usually detected by the winemaker and the tainted wine should not then reach the consumer. Examples of occurrence of organohalogen taints in foods and beverages are shown in Table 2.

Somewhat prophetically, Whitfield & others (1997) wrote that “the continued use of TBP, either as a fungicide or as a flame retardant, should be carefully monitored and a suitable alternative found before this compound and its metabolite TBA become costly food contaminants”. There have been several major food contamination incidents in Australia involving TBP since 1997, the latest as recently as August 2005.

**Recent international incidents**

Part of Brazil’s coffee production presents the so-called “Rio” defect characterised by a strong off-flavour often described as medicinal, phenolic or iodine-like. Spadone & others (1990) identified 2,4,6-TCA in concentrations ranging from 1–100 ppb, together with its precursor 2,4,6-TCP. The odour threshold of TCA in brewed coffee was found to be 8 ppt, and its taste threshold 1–2 ppt. Less than 50% of the TCA present in green beans was lost during roasting (Czerny & Grosch 2000). So far...
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...no explanation can be given for the presence of these compounds in coffee.

Polyethylene resin in Europe has been reported as becoming contaminated by halogenated phenols (in particular 2,4,6-tribromophenol) from several of the wooden pallets used to transport the resin from the manufacturer to the blow moulder (Eweder & others 1995).

The compound 2-bromo-4-methylphenol was identified as being responsible for a chemical phenolic taint in brine-salted Gouda cheese manufactured in New Zealand, the surface concentration ranging from 14–25 ppb. It was proposed that 4-methylphenol (which occurs naturally in cows’ milk) and active bromine could be the precursors. The salt used to make the brine had a concentration of 45 ppm of sodium bromide which could be converted to a reactive bromine species either by oxidation promoted by hypochlorite in the brine or by the generation of bromine radicals by UV light, as the brine is treated with hypochlorite and UV light to suppress yeasts and moulds (Mills & others 1997).

In 2000 the Taints and Off-Flavours laboratory at Reading Scientific Services (RSSL) in England issued a warning that the food industry could be heading for serious tainting problems caused by a new family of halogenated chemicals. This was prompted by increasing incidents of products being tainted by bromoanisole or iodophenols, such taints having hardly been heard of a few years ago although chloroanisoles have created a serious tainting problem for some time. RSSL quoted a case in which production was contaminated after the manufacturer received part-processed foodstuff shipped in a tainted vessel; the cost of cleaning the factory was approximately £0.75 million.

In 2003, Pira International Analytical Laboratory in England reported the identification of bromoanisoles as the cause of musty odour and chemical taste in packaging where previously it was due to the presence of chloroanisoles. They noted that until phenol-based wood preservers are discontinued, they will continue to be one of the most common, costly and easily preventable packaging-related causes of taint, and wooden pallets will remain high risk contaminating surfaces for packaging materials.

In 2004, Leatherhead Food Research Association in England reported an increase in the number of taints directly attributable to 2,4,6-TBP and 2,4,6- TCP which are used as wood preservatives. These compounds can also be converted to chloroanisoles or bromoanisoles which have been found in wood used in building storage facilities, pallets, soft wood crating and the floors of shipping containers.

Organohalogen taints are also produced in fruit juices by the soil-borne bacteria Alicyclobacillus species which were first isolated in 1982. In 1984 they were responsible for spoilage of large quantities of apple juice in Germany by producing 2,6-dibromophenol, 2,6-dichlorophenol and guaiacol. Control is difficult as they survive normal pasteurisation processes. Their growth is favoured when juice is stored at temperatures > 20°C (Chang & Kang 2004).

Other sources of taints

Organohalogen taints are not only a concern in food: earthy-musty off-flavour problems in municipal water supplies are due to organohalogen compounds present at the ppt level (Malleret & others 2001). TCA formation can easily occur in distribution systems and is linked mainly to fungi metabolism (Piriou & others 2001). The increasing use of high density polyethylene (HDPE) pipes to transport drinking water can lead to taints due to diffusion of organic additives from the polymer. Most of the chemicals identified in water had a basic common structure characterised by a phenolic ring typically substituted with hindered alkyl groups in positions 2 and 6 on the aromatic ring, the source of these compounds being attributed to impurities or by-products of typical phenolic additives used as antioxidants in the production of pipes (Brocca & others 2002). A major migrating component from HDPE pipes has been identified as 2,4-di-tert-butylphenol (Skjevrak & others 2003). Recently it has been shown that bromophenols are formed in drinking water from the reaction of phenol with hypobromous acid (HOBr) which is produced by oxidation of bromide with chlorine (Acero & others 2005).

The normal concentration of TCA in municipal water in North Ryde, Sydney (site of Whitfield’s laboratory) has been reported to be about 10 ppt and residents now apparently accept a slight ‘mustiness’ in their drinking water as a normal flavour (Whitfield & others 1987). This experience may well be replicated in many other cities. A plastic or chemical taint has recently emerged as a problem in drinking water in Perth. The taste occurs intermittently in zones receiving blends of treated groundwaters from several sources, but generally only in boiled water; the compound primarily responsible being 2,6-DBP (Heitz & others 2002). Musty taste in French drinking water was due to 2,4,6-TBA, caused by leaching of TBP from a storage tank with a cement-based coating and subsequent conversion by fungi to TBA (Malleret & Bruchet 2002).

In contrast to the organohalogen taints described above, organohalogen off-flavours have been identified in many seafoods. For example, 2,6-DBP has been
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Recent Australian experiences

Case study I – HDPE resin and milk

HDPE (high density polyethylene resin) was imported into Australia in 2005 in a shipping container as a bulk load with a low density polyethylene liner supported by fibreboard walls and floor. The resin spent approximately six weeks inside the container until it was unloaded and blow moulded into bottles which were then filled with milk. Consumer complaints resulted in a product recall and subsequent analysis of the resin and the affected milk revealed the presence of a range of organohalogenes as shown in Table 3.

With the exception of 4-bromophenol and 2,4-dibromophenol, all the halophenols detected in the contaminated HDPE resin exceeded their taste thresholds in water; six also exceeded their odour thresholds. In the milk, five compounds (2-chlorophenol; 2,4-dichlorophenol; 2,6-dichlorophenol; 2-bromophenol and 2,4,6-tribromophenol) all exceeded their odour and taste thresholds in water.

Table 2. Examples of organohalogen taints in foods and beverages.

<table>
<thead>
<tr>
<th>Incident</th>
<th>Cause</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eggs and broilers musty taint</td>
<td>Cage litter containing wood shavings treated with CPs</td>
<td>Engel &amp; others (1966)</td>
</tr>
<tr>
<td>Cocoa powder</td>
<td>Contaminated by CPs and CAs in paper sack linked to bleaching of pulp.</td>
<td>Whitfield &amp; others (1984)</td>
</tr>
<tr>
<td>Dried fruit musty taint</td>
<td>CPs in fibreboard cartons and wooden pallets after treatment with chlorine-based spray, then microorganisms forming anisoles.</td>
<td>Tindale &amp; Whitfield (1989)</td>
</tr>
<tr>
<td>Dried fruit musty taint</td>
<td>CAs from fungal conversion of CP in virgin and recycled fibreboard cartons.</td>
<td>Whitfield &amp; others (1991)</td>
</tr>
<tr>
<td>Imported champagne corks packed in polyethylene bags inside fibreboard cartons</td>
<td>Shipping container with wooden floor treated with TCP, then fungal methylation producing TCA, contaminating bags and corks.</td>
<td>Simpson &amp; Lee (1990)</td>
</tr>
<tr>
<td>Coffee found to contain TCP and TCA.</td>
<td>Cause not found in this case.</td>
<td>Spadone &amp; others (1990)</td>
</tr>
<tr>
<td>Canned beer musty taint</td>
<td>TCA absorbed into internal lacquer during transportation in shipping container.</td>
<td>Lambert &amp; others (1993)</td>
</tr>
<tr>
<td>Brine salted cheese phenolic taint.</td>
<td>4-methylphenol a natural component of cows’ milk was brominated by active bromine derived from brine solution.</td>
<td>Mills &amp; others (1997)</td>
</tr>
<tr>
<td>Bottled wine cork taint</td>
<td>TCA, TBA. Other compounds can be responsible e.g 2-methoxy-3,5-dimethylpyrazine(^a)</td>
<td>Buser &amp; others (1982), Sefton &amp; Simpson (2005), Simpson &amp; others (2004), Chatonnet &amp; others (2004)</td>
</tr>
<tr>
<td>Milk taint</td>
<td>Bottles blow moulded from imported high density polyethylene resin that had been contaminated by halophenols present in the container floor.</td>
<td>Australian dairy company (2005)</td>
</tr>
<tr>
<td>Canned beer musty taint</td>
<td>Empty can bodies shipped in container with TBA contaminated floor.</td>
<td>Australian brewery (2005)</td>
</tr>
<tr>
<td>Municipal water supplies earthy-musty off-flavour</td>
<td>Organohalogenes (TCA) at ppt levels</td>
<td>Malleret &amp; others (2001)</td>
</tr>
<tr>
<td>Drinking water</td>
<td>Diffusion of ‘phenolic’ additives (antioxidants) in polyethylene pipes</td>
<td>Brocca &amp; others (2002)</td>
</tr>
</tbody>
</table>

CP: Chlorophenol; CA: Chloroanisole; TCP: 2,4,6-Trichlorophenol; TCA: 2,4,6-Trichloroanisole;
\(^a\)2-Methoxy-3,5-dimethylpyrazine is also found in coffee and machine cutting emulsions (Mottram & others 1984).
Other pyrazines have been found as the cause of mouldy taint (Baille & others 1987).
Anisoles were detected, indicating that the container floor was probably quite dry. Although samples from the container floor were analysed, the results have not been released by the importer of the resin who commissioned the analysis.

To avoid repeat incidents, rigorous container inspection procedures prior to loading have been introduced by the resin supplier and a plastic foil laminate sheet is used to cover the container floor. In addition, sensory testing methods of incoming resin prior to unloading into silos at the blow moulding site have been upgraded.

**Case study II – canned beer**

Consumer feedback incidents in 2005 cited a musty aroma in a single brand of freshly canned beer and subsequent analysis identified TBA as the primary entity at levels between 10–40 ppt. Further investigations in the brewery identified the same musty taint in an unbroached pallet of empty can bodies. The can bodies were made in Australia and transported to the brewery by sea-freight – a journey lasting 10 days. Climatic conditions during transport and production periods were warm and humid (> 30°C and often > 60% RH over 14 consecutive days). Within four weeks of the main incident, multiple “micro” incidents (1–2 complaints) occurred across brands produced by multiple breweries. TBA was found in canned beer in these instances at concentrations of between 4–6 ppt.

An audit of the production facilities found no evidence of atmospheric TBA contamination within the packaging operations of the brewery. A number of fibre-based raw materials within the can manufacturing supply chain pool were assessed and found to contain TBP (Table 4). Specifically, TBP was found in moderate levels in fibreboard dividers, the paper stock used to make fibreboard dividers and the timber supply used to manufacture top frames and pallets. The shipping container used to transport the can bodies was tracked to the port of Jakarta and the timber floor found to contain TBA at very high levels (Table 4). This was the most likely origin of the main TBA taint in the batch of canned beer, the TBA and/or TBP arising either as residues from previous cargo or cleaning materials in combination with microbial methylation.

The occurrence of “micro” incidents was most probably due to a small number of heavily TBA-

### Table 3. Concentrations of organohalogenics in HDPE resin and milk\(^a\).

<table>
<thead>
<tr>
<th>Organohalogen</th>
<th>Odour threshold µg/L (ppb)</th>
<th>Taste threshold µg/L (ppb)</th>
<th>Resin</th>
<th>Milk</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Chlorophenol</td>
<td>0.4</td>
<td>0.1</td>
<td>0.4</td>
<td>0.9 - 3.36</td>
</tr>
<tr>
<td>4-Chlorophenol</td>
<td>20</td>
<td>39</td>
<td>n/d</td>
<td>n/d - 1.88(^b)</td>
</tr>
<tr>
<td>2,4-Dichlorophenol</td>
<td>0.4</td>
<td>0.3</td>
<td>2.1</td>
<td>1.14 - 12.59</td>
</tr>
<tr>
<td>2,6-Dichlorophenol</td>
<td>3.5</td>
<td>0.0062</td>
<td>9.6</td>
<td>n/d - 29.16</td>
</tr>
<tr>
<td>2,4,6-Trichlorophenol</td>
<td>300</td>
<td>2</td>
<td>3.0</td>
<td>n/d - 0.42(^b)</td>
</tr>
<tr>
<td>2-Bromophenol</td>
<td>0.1</td>
<td>0.03</td>
<td>0.7</td>
<td>0.28 - 1.07</td>
</tr>
<tr>
<td>4-Bromophenol</td>
<td>4</td>
<td>23</td>
<td>3.0</td>
<td>n/d - 0.01(^b)</td>
</tr>
<tr>
<td>2,4-Dibromophenol</td>
<td>0.5</td>
<td>4</td>
<td>1.3</td>
<td>n/d</td>
</tr>
<tr>
<td>2,6-Dibromophenol</td>
<td>0.1</td>
<td>0.0005</td>
<td>0.7</td>
<td>n/d</td>
</tr>
<tr>
<td>2,4,6-Tribromophenol</td>
<td>0.1</td>
<td>0.6</td>
<td>33.9</td>
<td>1.09 - 272</td>
</tr>
</tbody>
</table>

\(^a\) 12 different samples which gave rise to consumer complaints
\(^b\) Below odour and taste threshold concentrations in water
n/d = not detected

### Table 4. Concentration of organohalogenics in beer and packaging materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Beer A (ng/kg)</th>
<th>Beer B; C and D (ng/L)</th>
<th>Pallet timber</th>
<th>Local paper</th>
<th>Local divider</th>
<th>Imported divider</th>
<th>Container floor</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBA</td>
<td>10–40</td>
<td>4-6</td>
<td>-</td>
<td>20–370</td>
<td>n/d-160</td>
<td>3000</td>
<td>15 million</td>
</tr>
<tr>
<td></td>
<td>(ng/L)</td>
<td>(ng/L)</td>
<td></td>
<td></td>
<td>mean 40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TBP</td>
<td>-</td>
<td>-</td>
<td>260-17300</td>
<td>9100</td>
<td>7500-28200</td>
<td>8900</td>
<td>43 million</td>
</tr>
</tbody>
</table>
contaminated layer boards from the “main” incident being returned to the main pool of can body packaging materials. These boards carried enough TBA forward to subsequent production runs contaminating in a localised area the lining in a small number of can bodies. Of interest was the random detection of TBP within pallet timber. The results in Table 4 represent the scale of TBP present potentially due to environmental contamination as the timber mills sampled in this investigation did not employ TBP directly as a timber treatment.

Suggested solutions

The Australian government research organisation CSIRO has recommended a number of solutions over the last 20 years:

- Where biocides need to be used, they should be completely free of chlorophenols and their derivatives, and phenol and chlorine should never be used simultaneously for the sterilisation of plant and warehouse (Whitfield 1986).
- Container floors should be covered with an inexpensive disposable metal-plastic laminate film as a barrier to avoid chlorophenol contamination (Whitfield & others 1989).
- Only virgin kraft fibreboard with greatly reduced chlorophenol levels should be used in cartons for the packaging of dried fruit (Tindale & Whitfield 1989).
- Fibreboard cartons and timber pallets should be removed from storage areas before such areas are cleaned with agents containing hypochlorite and not returned until the areas are dry (Tindale & Whitfield 1989).
- Surfaces of pallets should be covered with a metal-plastic laminate foil to act as a barrier against possible contamination of foods by alien chemicals in timber (Tindale & Whitfield 1989).
- All shipping containers should have a foil laminate liner; layer divider boards should be of low moisture virgin kraft; and pallets should be lined with a foil laminate barrier material (Lambert & others 1993).

Precautions

Great care is necessary throughout the supply chain, from the specification of raw materials and packaging to the distribution of finished products, to minimise the risk of contamination. Three conditions are needed for materials to become contaminated through formation of anisoles: halophenol precursors, fungi and moisture. Therefore precautions should target the removal of at least one of these conditions. As well, steps must be taken to avoid contact with already contaminated materials.

The following list of precautions is based on various sources, but mainly from Whitfield (1986), and Maarse & others (1988). Some of these precautions relate to the precursors or “building blocks” of halogenated phenols (ie phenol and free halogens) or the halophenols themselves, and some to the conditions necessary for the biomethylation of halophenols to related anisoles. Precaution with regards to incoming goods, transport and distribution are especially important.

Incoming goods

1. Check that packaging manufacturers take steps to avoid the use of components containing free phenol, halophenols and their derivatives. Develop specifications accordingly (special attention has to be paid to recycled content in paperboard).
2. Monitor the level of halophenols in packaging materials, especially paperboard materials and adhesives. Fibreboard may contain various halophenols, most of which can only be detected by instrumental analysis. It is recommended that the quality of fibreboard used for transportation in bulk from overseas be monitored (eg fibreboard-made drums, large boxes), especially when the inner liner is not made from a barrier material.
3. Check the level of halophenols in doubtful pallets. Special attention has to be paid to one-way pallets used for transportation from overseas. The pallet supplier/manufacturer must guarantee and verify that all wood used for producing pallets was never treated with halophenols in the whole supply chain (but note that AQIS will treat all imported pallets with methyl bromide – see Pallet specifications p 13).
4. As a precaution, do not store imported pallets in areas where, if they are contaminated, they could transfer organohalogens to walls and other packaging materials.
5. Do not store packaging materials of natural origin (eg cardboard, wood, jute, cork) in high relative humidity environments (ie > 80%).
6. Ensure that pallets and corrugated boxes are removed from production areas prior to the use of chlorine-based sprays.
Processing

7. Where chlorinated water is used in the processing line or anywhere in the factory, thoroughly check all newly installed equipment, pipework and building materials for sources of phenolic compounds. Do not accept the installer's assurance.

8. Where process water is recycled to the boilers, make certain that it does not contain phenol or halophenols. In particular, establish that boiler water additives and wastewater from processing lines cannot provide a source of phenol when heated for prolonged periods in the boilers.

9. Make certain that any chlorophenol-based algaecides or disinfectants used in the factory cannot be accidentally introduced into the processing line. A critical step to avoid is cleaning with water containing phenol and chlorinated cleaning agents.

10. Choose insulation materials for the walls of chillers and cold stores with care, making certain that they do not contain phenol and have not been treated with halophenol fungicides.

11. Protect processed food against contamination by the environment. Do not store containers and bulk supplies in warehouses sited near chemical plants.

Transport and distribution

12. Use “food grade” shipping containers. Prevent stored packaged foods from coming into contact with timber previously treated with halophenol-based wood preservatives, fire retardants and anti-sapstain preparations. In particular, freight containers fitted with plywood floors can be contaminated with appreciable quantities of halophenols. A plastic foil laminate (PE or PP films are not barriers) can be used to prevent possible contamination by alien chemicals in the floor.

13. Never wash wood used in overseas transport (pallets, container floor) without subsequent complete and immediate drying. If such drying is not possible, eg in tropical climates, use only dry cleaning.

14. Take care that packaged products are not stored in contact with materials containing halophenols, even at low concentrations. The product can become contaminated with haloanisoles if storage conditions favour the growth of moulds able to methylate halophenols.

15. Cover the surfaces of pallets with a plastic foil laminate to prevent possible contamination by alien chemicals in the timber. This is a costly solution but is the only option when other preventive measures are difficult to implement.

16. Prevent condensation at the top of shipping containers by means of desiccants (condensation could occur particularly during the transportation of goods from a hot to a cold climate, when the cargo crosses the equator at high temperature and cools down afterwards).

Container specifications

Adhering to the practices within the Standards for Food Quality Shipping Containers publication from Shipping Australia Limited for container selection will minimise the risk of taints. Specifically the following points can help in the selection of acceptable containers:

- Reject any container which has debris or residue from previous cargoes, or shows any signs of mould growth.
- Reject any container which has free moisture on the walls or roof.
- Reject any container in which the floor timber has a moisture content of more than 22%.
- Dry-clean containers only, prior to loading. Do not wet-clean filthy containers, but rather reject them for ones in better condition.
- Do not load containers in inclement weather (rain, snow, etc) unless the area is sheltered. Products must enter the container in a dry condition.
- Avoid drastic temperature changes during loading, as this may cause condensation to occur.
- Avoid direct contact between cargo and container walls/door. Condensation is likely to occur in these areas. Putting dry, flat cardboard between the cargo and the walls/doors will help protect against condensation damage.
- Under no circumstances load a container with a damp floor or walls or roof.
- Reject any container in which an off-odour is detected.

Condensation

Temperature changes during transport may cause condensation. This will favour the growth of moulds which can convert halophenols to haloanisoles and thus affect the product’s taste and odour. Condensation may cause damage to outer packaging, eg rust on steel cans.

When a product is shipped from a warm to a cool climate, condensation may occur inside the walls of the container or under the stretch-wrap of the pallets,
increasing the relative humidity of the ambient air and creating ideal conditions for mould growth and corrosion of metallic packaging materials. Condensation can also take place when going from a cool to a warm climate when hot, humid air comes into contact with cold surfaces of any kind. The worst situation is when the container is opened and re-closed after inspection, with a delay of a few days before unloading.

Place Dribags (desiccants) in containers when necessary (e.g., hot to cold climate, crossing the equator, etc.), to avoid condensation or moisture damage.

Note: Palletised goods are usually stretch-wrapped with plastic film. The stretch wrapping must only be done if moisture levels and temperatures in pallets and cardboard are in equilibrium with ambient conditions. The recommended time to reach this equilibrium is five days.

**Moisture content of floors**

A shipping container should be rejected if the moisture content of the wooden floor is more than 22%.

The moisture content of the floor should be tested by taking six readings at the positions shown in Figure 2.

![Figure 2. Positions for moisture reading in a shipping container.](image)

The maximum reading for each container should be recorded; the container floor must have a moisture meter reading of no more than 22%.

A self-contained hand-held electrical resistance moisture meter with a 3 mm-pin type needle electrode is recommended for rapid determination of the moisture content of pallets and wooden container floors. These instruments have an accuracy of ±1% in the range of 6% to 24% moisture content and should be regularly calibrated using a crosscheck resistance card available from the meter suppliers, and the results recorded.

**Testing for odours**

Except for recently painted containers, most odours emanate from the wooden floor. Some are due to spillage, etc., from previous cargoes that have been absorbed by the wood and released over a period of time. Others, like musty odours, are produced by microbial action on substances in the wood. This latter type is accelerated by moisture in or on the floor and warm temperatures. Container floors, including repairs and replacements of wood, must not be treated with substances containing pesticides, halophenols or their derivatives. All odours released from the floor accumulate while the container is closed up.

Odour shall be assessed immediately the doors are opened. The door should be opened sufficiently to give entry and the decision made immediately. Containers that have been left opened for ventilation should be closed up for at least 24 hours before a reappraisal takes place. There shall be no harmful, offensive or persistent odours (e.g., phenol, paint, chlorine, solvent, disinfectant, chemical or musty) and all odours should have dissipated within 20 minutes of opening the container door.

- **If an off-odour is detected in any container, it must be rejected.**

It is difficult to ensure that suppliers of raw materials or packaging will carry out a rigorous inspection of containers prior to loading. In such cases, it is prudent to require such suppliers to line the floor of the container with a plastic foil laminate material. Without this liner, there can be no guarantee that tainting will not occur.

**Pallet specifications**

PCP (pentachlorophenol) is the main halophenol in wood. From a tainting perspective, PCP is not an essential compound; however, it is always accompanied by residues of less substituted phenols, including the most critical one: 2,4,6-TCP. It is recommended that PCP, TCP and TBP in pallets be monitored, especially for timber originating from certain parts of the world (Eastern Europe, Northern Asia). For wood, it is more efficient to check for the presence of halophenols (precursors of related anisoles) rather than haloanisoles.

**CHEP®** (“blue”) pallets are made from Australian hardwood and are not treated with any timber preservative; they can be considered as reliable material. **Loscam®** (“red”) pallets are manufactured in Victoria from untreated sash or radiata pine and can also be considered as reliable. Assume that all imported pallets have been treated with preservatives.
Suspect or at-risk pallets used to transport raw materials, packaging and finished product require a plastic foil laminate material to cover the pallet. Without this cover, there can be no guarantee that tainting will not occur.

AQIS fumigate all wooden pallets entering Australia with methyl bromide. Details of this procedure can be found in the AQIS Methyl Bromide Standard version 2 March 2005 (www.aqis.gov.au/content/publications). In theory (and therefore maybe in practice), methyl bromide could react with TBP under basic conditions via a methylation reaction to produce TBA.

International Standards for Phytosanitary Measures are published by the Secretariat of the International Plant Protection Convention of the Food and Agriculture Organisation of the United Nations, their Guidelines for Regulating Wood Packaging Material in International Trade having been published in March 2002 (www.ippc.int). This provides details of the treatments required for wooden packaging materials such as pallets used in international trade. For such wooden items imported into Australia, the AQIS standard referenced above applies.

Actions once contamination has occurred

Unfortunately, when food or food packaging is tainted with organohalogenes, there is no other solution than to destroy the affected lot of product (an exception is the cork industry which has introduced a process to remove anisoles using supercritical CO$_2$). In particular, the dilution of a tainted food in order to lower the concentration of haloanisole(s) under the threshold level(s) should never be countenanced as the conversion of phenols into anisoles by fungal methylation (a slow process) could still be going on and the risk of a later tainting of an even greater quantity of food cannot be excluded.

Conclusion and recommendations

Tainting of any component within the ingredient and packaging supply chain may lead to a taint in the packaged food.

- TBP used either as a preservative, fungicide or fire retardant poses on-going risks to food contamination.
- Recycled timber, paperboard products and polymer plastics provide a source of potential taint compounds.
- Timber pallets and the floors in shipping containers should be closely assessed for taints and, where necessary, covered with a plastic foil laminate barrier as a precaution.
- Environmental taint potential should be assessed adopting Hazop protocols within a production facility.
- TCP and TBP levels within the material supply chain should be managed to defined levels within a QA program.
Organohalogen Taints in Foods

References


