
CODE OF PRACTICE FOR THE REDUCTION OF 3-
MONOCHLOROPROPANE-1,2-DIOL (3-MCPD) DURING THE
PRODUCTION OF ACID-HVPs AND PRODUCTS
THAT CONTAIN ACID-HVPs

CXC 64-2008

INTRODUCTION

1. 3-Monochloropropane-1,2-diol (3-MCPD) is one of a series of compounds referred to as chloropropanols. These compounds are contaminants that are formed during the processing and manufacture of certain foods and ingredients. They were originally discovered in acid hydrolysed vegetable protein (acid-HVP) in the 1980s. Subsequent research in the 1990s revealed their presence in soy sauces manufactured using acid-HVP as an ingredient.
2. Acid-HVPs are produced *via* the hydrolysis of various proteinaceous vegetable and animal materials with hydrochloric acid. They are used widely as flavour enhancers and as ingredients in processed savoury food products and pre-prepared meals. Typical levels in foods range from *ca.* 0.1 to 20%.
3. The occurrence of chloropropanols in acid-HVP arises from their formation during the hydrochloric acid mediated hydrolysis step of the manufacturing process. During this hydrolytic stage the acid also reacts with residual lipids and phospholipids present in the raw material, resulting in the formation of chloropropanols. It has been industry experience that chloropropanol formation cannot be avoided through the use of defatted protein sources.
4. In addition to formation of chloropropanols during the manufacture of acid-HVP for use as an ingredient, chloropropanols may also be formed in those soy sauces, and related condiments, where the manufacturing process of the sauce itself includes hydrochloric acid treatment of soybean meal. As with acid-HVP the mode of formation also involves acidic hydrolysis of residual lipids and phospholipids.
5. A range of techniques may be employed in the manufacture of soy sauces. Generally, products made exclusively by means of fermentation do not contain chloropropanols, or, if present, they only occur in trace amounts. It is those products that utilise acid-HVP as an ingredient that may contain chloropropanols. Soy sauces, and related products, that are subject to acid treatment during manufacture may also contain chloropropanols.

6. Generally, 3-MCPD is the most widely occurring chloropropanol in foods that contain acid-HVP. It is present as a racemic mixture of (*R*) and (*S*) isomers in protein hydrolysates. Other chloropropanols that can occur, albeit usually in smaller amounts, are 2-monochloropropane-1,3-diol (2-MCPD), 1,3-dichloro-2-propanol (1,3-DCP) and 2,3-dichloro-1-propanol (2,3-DCP).
7. The presence of chloropropanols in food is of concern owing to their toxicological properties. The Joint FAO/WHO Expert Committee on Food Additives (JECFA) considered 3-MCPD and 1,3-DCP in June 2001 and assigned a provisional maximum tolerable daily intake (PMTDI) for 3-MCPD of 2 µg/kg bw/day. The Committee re-evaluated chloropropanols in June 2006 and decided to retain the previously established PMTDI. On evaluating 3-MCPD, the Committee commented that reduction in the concentration of 3-MCPD in soy sauce and related products made with acid-HVP could substantially reduce the intake of this contaminant by consumers of these condiments.
8. Different regional markets may require products with different organoleptic qualities to accommodate specific regional tastes. The individual approaches and combinations thereof, outlined later in this document, to minimise levels of 3-MCPD will have different effects on the organoleptic qualities of the final product and as such, manufacturers should take these effects into account when selecting a strategy to minimise 3-MCPD formation. Whilst it is technically possible to reduce 3-MCPD levels to below 0.1 mg/kg, the organoleptic qualities of such products may be adversely affected as the flavour and taste (umami) directly reflect the quality of the acid-HVP. This is particularly true in aged acid-HVP products.
9. Manufacturers have implemented measures to reduce the levels of chloropropanols in acid-HVPs and related products. Details of the general procedures used to manufacture acid-HVPs with low levels of chloropropanols are given in the following section. Some manufacturers undertook reformulation of their products during the early 1990s so that the effects of changes in organoleptic properties experienced when using the improved methods of manufacture could be minimised. Other production processes resulted in products with lower levels of chloropropanols whilst minimising the effect on organoleptic properties. Implementing manufacturing procedures to reduce 3-MCPD in acid-HVP to low levels can be technically difficult and very expensive, often with new equipment being required. Reformulation of the recipes for processed foods made using acid-HVP may also be necessary.
10. Chloropropanols have also been detected in a range of other foods that are not subject to acid hydrolysis during manufacture. These foods include processed fruits and vegetables, cereals and bakery products, processed meats, smoked fish and beer.

SCOPE

11. The purpose of this Code of Practice is to describe and disseminate best practice for the manufacture of acid-HVP and soy sauces and related condiments, whose production involves acid hydrolysis, with the aim of facilitating a reduction in the levels of 3-MCPD. Food ingredients produced using methods that do not involve acid hydrolysis of vegetable proteins are not covered by this Code of Practice.

RECOMMENDED PRACTICES BASED ON GOOD MANUFACTURING PRACTICE (GMP)

Acid-HVPs

12. The manufacturing process for acid-HVPs will vary depending on the desired organoleptic properties of the end product. The source of the raw material, molarity of the acid, temperature of the reaction, time of the reaction and other factors can all affect the organoleptic properties of the final product. A generalised description of the acid-HVP manufacturing process can be given (see fig. in Annex). Common vegetable raw materials used in the production of acid-HVP include defatted oil seeds (soy and peanut), and protein from corn maize, wheat, casein, yeast and rice. These are hydrolysed with hydrochloric acid ranging from below 4 M to 9 M, at a temperature between 70 °C and 135 °C for up to 8 hours, although times of up to 20–35 hours have been reported, at pressures usually greater than atmospheric pressure. After cooling, the hydrolysate is neutralised with either sodium carbonate or sodium hydroxide to a pH of 5 to 9 at a temperature between 90 to 100 °C for 90 to 180 minutes and then hydrochloric acid is added to the mixture to adjust the pH to between 4.8 and 5.2. The hydrolysate is filtered to remove the insoluble carbohydrate fraction (humin) and then bleached or refined. Activated carbon treatment can be employed to remove both flavour and colour components, to the required specification. Following further filtration, the acid-HVP may, depending upon the application, be fortified with additional flavouring components. Thereafter, the product can be stored as a liquid at 30–50% dry matter (corresponding to 2–3% total nitrogen), or alternatively it may be vacuum dried, spray-dried, or steamed and stored as a solid (97–98% dry matter).

Methods that can be employed to reduce the levels of 3-MPCD in acid-HVP

13. Three main approaches may be adopted to minimise the concentration of 3-MCPD in the final product. The first of these involves careful control of the acid hydrolysis step; the second, subsequent neutralisation to minimise 3-MCPD formation; and the third employs the use of sulfuric acid as a substitute for hydrochloric acid in the hydrolysis step. These methods can reduce the levels of 3-MCPD in acid-HVPs.

14. Manufacturers should consider the three options below and decide which are most suitable for their method of acid-HVP production. The three approaches are detailed in the following paragraphs, with specific examples given. These approaches are based on a limited amount of information that is available in the public domain; therefore, it has not been possible to provide a full account of how to manufacture low 3-MCPD acid-HVP. The information that follows is general advice; at the national level, manufacturers may need to adjust the measures in their own production processes.
15. With regard to the first strategy, the temperature and the heating time of the acid hydrolysis step must be simultaneously controlled and careful attention paid to the reaction conditions in the subsequent neutralisation step. Typically, the hydrolysis reaction is initially carried out at a temperature between 60 and 95 °C for up to 150 minutes. The temperature of the reaction is then increased gradually until a temperature of 103–110 °C is attained. Once this maximum temperature is reached, it should be maintained for 2–35 hours and then the resulting hydrolysate cooled over 3 hours, neutralised and filtered. Careful control of the acid hydrolysis step has been shown to reduce levels of 3-MCPD in the hydrolysate to below 10 mg/kg.
16. 3-MCPD that is formed during the acid hydrolysis step may be removed by a secondary alkaline hydrolysis. This alkaline treatment is, in essence, an extension of the neutralisation process that follows acid hydrolysis of the starting material; it causes degradation of the chloropropanols present in the hydrolysate. The alkaline treatment can be performed before or after filtration of the hydrolysate, although alkaline treatment is preferable before filtration because the residue will also then be free of 3-MCPD. The hydrolysed protein is treated with food-acceptable alkali such as potassium hydroxide, sodium hydroxide, ammonium hydroxide or sodium carbonate to increase the pH to 8–13. This mixture is then heated in the range 110–140 °C for up to 5 minutes, other reported conditions involved heating in the range 60–100 °C for 90–900 minutes. Generally, alkaline treatments at higher pH and temperature will require shorter processing times. After cooling, the pH of the resulting hydrolysate should be alkaline (ideally above pH 8 at 25 °C); if the pH is lower, the treatment was most probably not effective and corrective measures should be taken. Following alkaline treatment, the pH of the hydrolysed protein is readjusted to a pH of 4.8–5.5 using a suitable acid (e.g. hydrochloric acid) at a temperature of 10–50 °C. The hydrolysate may now be filtered to remove any insoluble residues and the final product obtained. Use of an alkaline treatment when manufacturing acid-HVP has been shown to yield a final product with 3-MCPD levels below 1 mg/kg. It should be noted that a harsh alkaline treatment will reduce the organoleptic qualities of the final products; therefore, it is advised to start the alkaline treatment with a hydrolysate with low levels of 3-MCPD, which can be achieved through careful control of the acid hydrolysis step. Of course, it is important to pay attention to possible recontamination if secondary alkaline

hydrolysis is used to further reduce the 3-MCPD content of acid-HVP produced by careful control of the acid hydrolysis step. The alkali treated hydrolysate (with low levels of 3-MCPD) must be kept away from equipment (e.g. reaction vessels, pipes, pumps and filter presses) that is used when performing the initial acid hydrolysis step.

17. It is possible to manufacture acid-HVP using sulfuric acid, thus eliminating the presence of chloride ions that lead to the formation of 3-MCPD. Soybean meal and sulfuric acid are mixed together for 8 hours at a pressure of 10 psi. The resulting hydrolysate is neutralised and the final product is filtered and washed. The diminished organoleptic properties of sulfuric acid-HVP are improved by combination of the final product with flavourings (e.g. monosodium glutamate, caramel, disodium inosinate, disodium guanylate and lactic acid).

Soy sauces and related products

18. A number of different manufacturing processes are employed in the production of soy sauces and the method used will impact on whether the product contains 3-MCPD.

Soy sauces produced by fermentation

19. Soy sauces that are produced solely by fermentation contain non-quantifiable or, in rare cases, extremely low levels of 3-MCPD. Soybeans (whole or defatted) and other cereal grains such as wheat are the main ingredients used for naturally fermented soy sauce. At the start of the process these materials are pre-cooked, mixed and inoculated with *Aspergillus oryzae* and/or *Aspergillus sojae*. After incubation for 1 to 3 days, at 25–30 °C, salt water is added and the mixture is fermented and aged at a temperature below 40 °C for not less than 90 days. Short-term fermented soy sauce is produced in a similar manner except that the salt water fermentation/ageing stage takes place at or above 40 °C and the process is completed within 90 days.

Soy sauces whose manufacture involves an acid treatment stage

20. Alternatively, soy sauces may be manufactured using acid-HVP and other ingredients such as sugars and salt. These products may contain 3-MCPD and measures to prevent its occurrence are described above for acid-HVP. Use of these processes will yield products with low levels of 3-MCPD.
21. A further manufacturing technique involves mixing fermented soy sauces with those derived from acid-HVP. Manufacture of some products involves ageing after mixing. Such products (commonly known as semi-chemical soy sauces) may also contain 3-MCPD and appropriate measures to minimise its presence in the acid-HVP are described earlier.

ANNEX

MANUFACTURING PROCESS OF ACID-HVP AT COMMERCIAL SCALE

