Printed in the Republic of Korea
ANALYTICAL SCIENCE & TECHNOLOGY
Vol. 21, No. 6, 543-552, 2008

# A sensitive analytical method for determination of 3-monochloropropane-1,2-diol and 1,3-dichloropropan-2-ol in various foods by gas chromatography with mass spectrometer

**Eunju Kim, Sungkug Park and Dongmi Choi★**

*New Hazard Chemicals Division, Department of Food Safety Evaluation, Korea Food & Drug Administration*
*231 Jinheung-no Nokbun-dong Eunpyung-ku, Seoul, 122-704, Korea*
(Received December 4, 2008, Accepted December 12, 2008)

# 가스크로마토그래피/질량분석기를 이용한 식품 중 클로로프로판올 화합물 분석

**김은주 · 박성국 · 최동미★**

식품의약품안전청 신종유해물질과
(2008. 12. 4. 접수, 2008. 12. 12. 승인)

**Abstract:** This paper described the relatively sensitive and simultaneous analytical method for 3-monochloropropane-1,2-diol (3-MCDP, $C_3H_7ClO_2$, MW. 110) as well as 1,3-dichloropropan-2-ol (1,3-DCP, $C_3H_6Cl_2O$, MW. 128) in various foods. Food samples were homogenized in 5M NaCl solution, mixed with aluminum oxide and eluted with dichloromethane. The extracted chloropropanols were concentrated by rotary evaporator and $N_2$ blow serially were derivatized with HFBA (Heptafluorobutyric anhydride, $C_8F_{14}O_3$, MW. 410) and were determined by GC/MS using isotope dilution method. The characteristic molecular ions at m/z 253, 275, 289, 291, and 453 for HFBA derivatives of 3-MCPD (MW. 502) and 110, 275, and 277 for HFBA derivatives of 1,3-DCP (MW. 325) were chosen in selected ion mode. The method validation data showed sufficiently good properties of LOD (0.003 mg/kg), LOQ (0.010 mg/kg), linearity ($R^2 \geq 0.999$ at 0.010~1.000 mg/kg), and recovery rate ($\approx$97%). The levels of chloropropanols in soy sauce, sauces, processed meat products, fishery products, and seasonings (n=56/157) determined by the presented method were 0.0~0.3 mg/kg.

**요 약:** 식품 중 클로로프로판올 화합물인 3-MCPD (3-monochloropropane-1,2-diol, $C_3H_7ClO_2$, MW. 110) 및 1,3-DCP (1,3-dichloropropan-2-ol, $C_3H_6Cl_2O$, MW. 128)를 분석하는 효과적인 방법을 확립하였다. 시료를 5M NaCl용액으로 균질화 한 후 알루미늄옥사이드와 섞어 유리컬럼에 충진하고 디클로로메탄으로 시료 중 클로로프로판올 화합물을 용출하였다. 용출된 클로로프로판올 화합물은 감압증류장치와 질소가스로 농축한 뒤 HFBA (Heptafluorobutyric anhydride, $C_8F_{14}O_3$, MW. 410)로 유도체화하여 GC/MS로 분석하였다. 3-MCPD-HFBA 유도체화 화합물(MW. 502)은 m/z 253, 275, 289, 291, 453를 선택이온으로 하고 1,3-DCP-HFBA 유도체화 화합물(MW. 325)은 110, 275, 277를 선택이온으로 설정하여 정성 · 정량 하였

★ Corresponding author
Phone : +82-(0)2-380-1664 Fax : +82+(0)2-382-4892
E-mail : mechoi@kfda.go.kr

다. 확립된 분석법의 정량한계는 3-MCPD 및 1,3-DCP 모두 0.01 mg/kg이었고, 0.01~1.00 mg/kg의 농도 범위에서 직선성($R^2 \geq 0.999$)이 좋았으며 평균회수율은 약 97%내외였다. 확립된 분석법을 이용하여 다양한 식품 중 클로로프로판올 화합물을 조사한 결과, 0.0~0.3 mg/kg (n=56/157) 수준으로 3-MCPD로 검출되었다.

**Key words :** 3-monochloropropane-1,2-diol, 1,3-dichloropropan-2-ol, Analytical method, Survey

## 1. Introduction

Chloropropanol compounds such as 3-monochloropropane-1,2-diol (3-MCPD) and 1,3-dichloropropane-2-ol (1,3-DCP) are well known chemical contaminants which were first recognized as byproducts during processing procedure of acid hydrolyzed vegetable protein (HVP) in 1980's.[1] Formation of 3-MCPD is a result of°°the replacement of fatty acid attached on glycerol backbone of triglyceride from vegetable proteins with chloride supplied from hydrochloric acid. Another chloropropanol compound, 1,3-DCP, can be formed from 3-MCPD as a result of progressive chlorination of residual lipids originated from vegetable proteins at high temperature.[2] Chloropropanol compounds are mostly found in soy sauces made with acid hydrolysis of protein and foods containing HVP made by extraction of protein from defatted vegetable protein by acid hydrolysis. Recent survey report showed that chloropropanols have been detected in various food items including processed fruits and vegetables, cereals, bakery products, processed meat, and smoked fish which were not subject to acid hydrolysis during manufacture.[3-8]

3-MCPD was defined as a genotoxic carcinogen by the European Commission's Scientific Committee for Food in 1997 while the Joint Food and Agriculture Organization/World Health Organization Expert Committee in Food Additive (JECFA) concluded 3-MCPD is a non-genotoxic carcinogen in *vivo* based on reviewed new toxicicological data and determined 2 μg/kg·wt of provisional maximum tolerable daily intake (PMTDI) for 3-MCPD in 2001.[9] Committee on Carcinogenicity of Chemicals in Food (COC) classified 1,3-DCP as a potentially genotoxic carcinogen *in vivo*[10] and JECFA confirmed TDI for 1,3-DCP could not be determined due to its genotoxic carcinogenicity. However, JECFA concluded management of 1,3-DCP would be carried on by controlling 3-MCPD because only severe contamination of 3-MCPD relating to contamination of 1,3-DCP.[9] There is controversial idea regarding 3-MCPD as an animal carcinogen because one study showed 3-MCPD caused formation of tumors in kidney of rat 344[11] while the other study did not result in abnormal synthesis of micronucleus (bone mallow) and unscheduled DNA(liver) of rats due to 3-MCPD oral dose.[12] International agency for Research on Cancer (IARC) does not recognize 3-MCPD and 1,3-DCP as carcinogens but their levels in food should be reduced to levels as low as technically possible.[10]

Qualification as well as quantification of 3-MCPD have been done in its derivatized or un-derivatized form using gas chromatography/mass spectrometer (GC/MS) in general. There is research done to improve sensitivity and selectivity of detection for mono-chloropropandiols by using different detectors, extracting solvents, derivatization chemicals, and etc. Detection of 3-MCPD was improved by using electrolytic conductivity detector in halogen mode.[13] 3-MCPD was determined by flame ionization detector after derivatization with phenylboric acid with 0.2 mg/kg of detection of limit (LOD).[14] Kissa determined 3-MCPD derivative of N, O-bis (trimethylsilyl) trifluoroacetamide using GC with flame ionization detector.[15] Mono-chlororpandiols such as 3-MCPD and 2-MCPD (2-chloro-1,3-propandiol) in HVP, seasonings, bread, meat, and starch were determined in forms of their HFBI (heptabutylrylimmidazole) derivative using GC/ion trap tandem MS.[16] The study presented a rapid and resolute analytical method

where mono-chloropropandiols extracted with diethyl ether and derivatized with toluene-4-sulfonic acid monohydrate were determined using GC/MS/MS.[17] However, the literature for simultaneous separation and determination of chloropropanols such as 3-MCPD and 1,3-DCP at low μg/kg levels is limited.[18] Brereton and his colleague developed the analytical method where 3-MCPD in a wide range of food was determined using deuterated internal standard by GC/MS and validation of the method was done by asking 12 laboratories to quantify of 3-MCPD. The results from inter laboratory analysis satisfied with quantification of 3-MCPD at levels of ≥0.01 mg/kg and the presented analytical method was adapted First Action of AOAC international.[19] Crew and others extended Brereton and other's analytical method with incorporation of cryogenic trap and GC column to increase intensity at the level of 0.003 mg/kg of detection limit for 1,3-DCP.[20] Other study showed that chloropropanols including 3-MCPD and 1,3-DCP in soy sauces were determined by GC/MS with derivatization of HFBA (heptafluorobutyric anhydride). Validation of the method resulted in about 5 μg/kg of LOD for both chloropropanols and 77 and 98% of recoveries for 3-MCPD and 1,3-DCP respectively.[18] Others determined 3-MCPD as well as 1,3-DCP in soy sauce, cereals, rice crackers, soup, soup powder and malt extract using disposable reservoirs packed with aluminum oxide which were replaced with extraction-columns such as glass-column or Extrelut® etc.[21]

The improvements in detection of chloropropanols at low μg/kg level by modification of previous analytical methods and survey of chloropropanols in various foods were the objective of this research.

## 2. Experimental

### 2.1. Chemicals

#### 2.1.1. Reagents and materials

3-chloro-1,2-propandiol (3-MCPD) was purchased from Sigma-Aldrich Co. (St. Louis, US) and 1,3-dichloropropane-2-ol (1,3-DCP) was purchased from Fluka Co. (Carlo Erba, France). The internal standards (3-MCPD-*d5* and 1,3-DCP-*d5*) were obtained from CDN Isotope Co. (Pointe-Claire, Canada). Reagent chemicals such as aluminum oxide, sodium sulfate anhydrous, and heptafluorobutyric anhydride (HFBA) were purchased from Sigma-Aldrich Co. (St. Louis, US) and the used solvents such as water, ethyl acetate, dichloromethane, ether, and isooctane were HPLC grade (Merck Co., Damstadt, Germany).

The various foods including soy sauces, sauces, curry powder, processed meat and fishery products, and other foods were purchased from grocery markets in Korea.

#### 2.1.2. Standard solutions

Stock solutions of external standards for 3-MCPD and 1,3-DCP and internal standards for 3-MCPD-*d5* and 1,3-DCP-*d5* were prepared at appropriated concentration by dissolving the standards in ethyl acetate and stored at room temperature. External standard solutions were prepared for calibration at a concentration range of 0.01~1.0 μg/kg concentrations by mixing each external standard stock solution and diluting the mixture with ethyl acetate. The mixed internal standard solution of 3-MCPD-*d5* and 1,3-DCP-*d5* was prepared at 1.0 μg/kg by mixing each internal standard stock solution and diluting the mixture with ethyl acetate.

### 2.2. Sample preparation

#### 2.2.1. Elution solvent selection

One of each from solid (seasoning powder), liquid (soy sauce) and paste food (soup) was chosen and to be eluted with solvent such as dichloromethane, ethyl acetate, and diethyl ether for eluting samples for selecting extracting solvent. The procedure of sample preparation was optimized by adjusting amount of aluminum oxide as a packing material and volume of the selected organic solvent as extracting material.

#### 2.2.2. Extraction

The homogenized sample (5 g) massed-up with 5M sodium chloride solution to 30 mL was placed into a 50 mL screw-cap test tube and sonicated for

10 min. The sonicated 2 mL of upper solution was mixed with approximate 4 g of aluminum oxide after spiking 10 μL of internal standard solution. The mixture of sample and aluminum oxide was packed into a glass column (25 mm × 300 mm) and top of the packed mixture was covered with small amount of sodium sulfate anhydrous. The packed mixture was eluted with 30 mL of dichloromethane at a rate of 2 mL/min and eluent was collected in a 100 mL pear-shaped flask. The dichloromethane eluent was concentrated to about 1 mL by using a rotary evaporator in water bath (30°C) and transferred into a 15 mL screw-cap test tube. The flask was washed with 10 mL of dichloromethane and washing solution was added into a screw-cap vial. The primary concentration with washing solution was further concentrated to almost dryness under nitrogen gas. If sample contained much fat or lipid, the packed mixture was eluted with 30 mL of hexane first and then followed the procedures presented in above.

#### 2.2.3. Derivatization

The residual concentrate was dissolved with 1 mL of isooctane and derivatized with 150 μL of HFBA in a screw-cap test tube at 60°C for 30 min. The reacted test tube was cooled down to the room temperature, mixed on vortexer after adding 5 mL of distilled water, and then set to be separated organic and aqueous phase. The organic phase was transferred into a test tube containing small amount of sodium sulfate anhydrous and filtered with 0.45 μm of PVDF filter before injecting to analysis for GC/MS.

### 2.3. Analytical method

#### 2.3.1. Apparatus condition

GC/MS analysis was carried out using a gas chromatograph equipped with mass spectrometer (1200 Triple Quadrupole GC/MS, Varian Co., Palo Alto, US) in the EI mode at electron energy of 70 eV and source temperature of 230°C. The separation of chloropropanol derivatives was done on DB-5MS column (30 m × 0.025 mm, 0.25 μm, Agilent J & W Scientific Inc., Folsom, US) with carrier gas of He at a constant flow of 0.8 mL/min, split ratio of 20:1, and injector temperature of 250°C. The temperature program for GC column was set : initial temperature of 50°C held for 5 min, increased to 90°C at a rate of 2°C/min and held for 5 min, and then increased up to 280°C at a rate of 30°C/min and finally held for 3 min. Qualitative and quantitative analysis was done by selective ion monitoring (*Table* 1).

#### 2.3.2. Chloropropanol determination

The retention time of TIC (Total Ion Chromatogram) from standard and sample should agree within ± 0.2 min for confirmation of both 3-MCPD and 1,3-DCP. The ratios of the responses at m/z 253, 275, 289, and 291 relative to the response at m/z 453 in standard and in sample were compared and at least 2 of the 4 ion ratios should be with in ±20% of the mean of the ion ratios of standards for confirmation of 3-MCPD. The ratios of the responses at m/z 275 relative to the response at m/z 277 and 110 should be with in ±20% of the mean of the ion ratios of standards for confirmation of 1,3-DCP.

#### 2.3.3. Chloropropanol quantification

The calibration curve for 3-MCPD was constructed by plotting the ratios of 3-MCPD derivative peak area at m/z 253 to 3-MCPD-*d5* derivative peak area at m/z 257 versus the concentrations in μg/kg of 3-MCPD. The calibration curve for 1,3-DCP was constructed by plotting the ratios of 1,3-DCP derivative peak area at m/z 275 to 1,3-DCP-*d5* derivative peak

*Table* 1. Characteristic ions selected in the EI mass spectra of HFBA derivatives of chloropropanols

| Compound | HFBA Derivatives (M.W) | Ions selected | Qualifier | Quantifier |
|---|---|---|---|---|
| 3-MCPD | 502 | 253 275 289 291 453 | 453 | 253 |
| *d*5-3-MCPD | 507 | 257 278 294 296 456 | 456 | 257 |
| 1,3-DCP | 325 | 275 110 277 | 277 | 275 |
| *d*5-1,3-DCP | 329 | 278 280 116 | 116 | 278 |

at m/z 278 versus the concentrations in μg/kg of1,3-DCP. The computed area ratios from chromatograms of samples were quantified by the calibration curve.

### 2.4. Chloropropanols in food

The levels of 3-MCPD and 1,3-DCP in various food items which were purchased from local grocery markets in Korea were determined by the presented analytical method in above.

## 3. Results and Discussion

### 3.1. Sample preparation

The amount of aluminum oxide was determined depending on its capacity moisture absorbance and mixing efficiency with sample in a practical manner. The ratio 2:1 of aluminum oxide to sample was used because it was appropriate for solvent extraction as well as moisture absorbance (data not shown). The solvents were evaluated for their extraction capacity by comparing their recovery rates of chloropropanols (*Fig.* 1). The tested solvent efficiencies for extraction of 3-MCPD as well as 1,3-DCP were dependent on types of food matrix. Dichloromethane resulted in better 1,3-DCP extraction in various food matrix and relatively similar extraction efficiency for 3-MCPD compared to those of other solvents. The ethyl acetate eluant resulted in the less 1,3-DCP while more 3-MCPD compared to others. Our results partially agreed with that of Ushijima *et al*. They reported ethyl acetate showed better extraction of 3-MCPD than diethyl ether in aqueous samples.[22] Chung *et al.* reported the interference of co-eluted compound which resulted in the same spectra at m/z

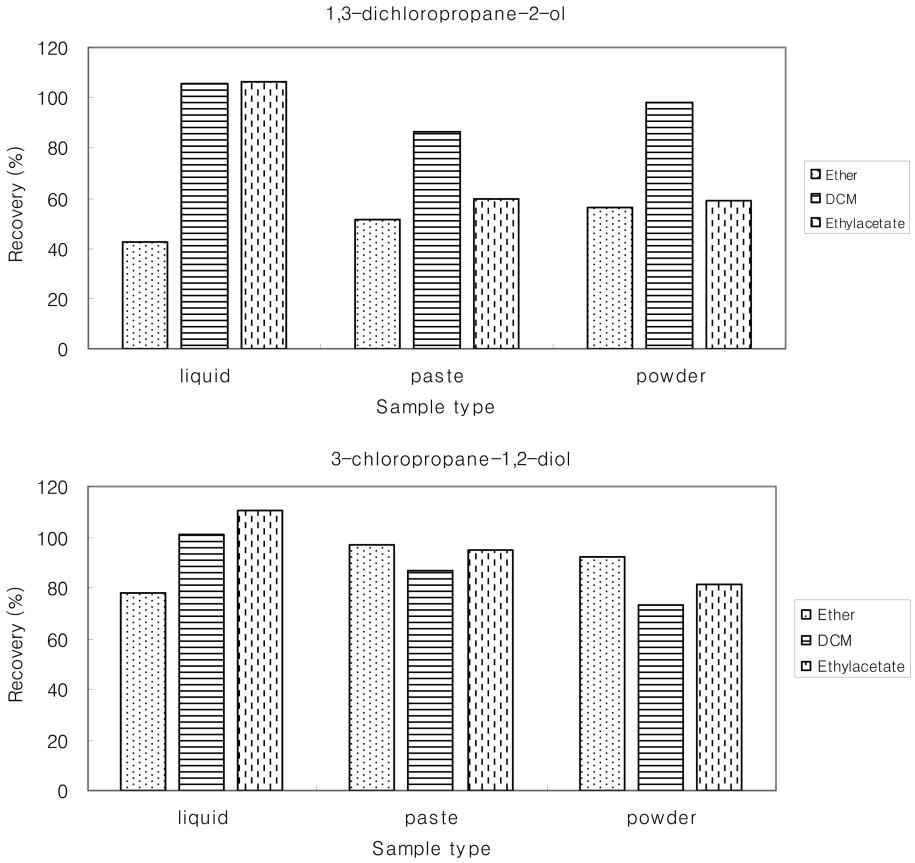


*Fig.* 1. The effect of different solvents on chloropropanol extraction in various foods.

*Table* 2. The effect of dichloromethane volume on the extraction of chloropropanols

| Solvent volume (mL) | Recovery rate (%) | |
|---|---|---|
| | 3-MCPD (CV%) | 1,3-DCP (CV%) |
| 30 (n=6) | 91.7 (3.9) | 93.8 (6.4) |
| 50 (n=6) | 91.9 (5.8) | 92.3 (7.3) |

253 and 275 compared to those of 3-MCPD.[18] The other study reported that the determination of 1,3-DCP in food containing HVP was subject to false-positive results applied with HFBI derivatization after mixing sample with a sodium chloride solution and extracting with diethyl/hexane.[23] In the present study, ethyl acetate extraction showed that the response abundance of co-eluted materials at m/z 275 (1,3-DCP quantifier) was noticed resulting overestimation of 1,3-DCP in several samples. Therefore, dichloromethane was chosen for sample extraction nevertheless ethyl acetate showed better 3-MCPD extraction. The effect of solvent volume on chloropropanol extraction was presented (*Table* 2). The extraction capacity of chloropropanols was not significantly affected by dichloromethane volume. The 3-MCPD recovery (%) with 30 mL and 50 mL of dichloromethane extraction were 97.1 and 98.8%, respectively. The 1,3-DCP recovery (%) with different volume of dichloromethane were similar to those of 3-MCPD, which were 96.9% for 30 mL extraction and 97.3% for 50 mL extraction. It could be induced that 30 mL of dichloromethane was relatively sufficient to extract chloropropanols in samples.

Acylation, akylation, and silylation are commonly used methods to derivatize and analyze chloropropanols incorporated with GC/MS. The use of HFBA or HFBI forms heptafluorobutyryl derivatives of chloropropanols by acylation resulting in hydrolytically stable compounds in spite of relatively difficult preparation.[16,19,24] The use of phenyl boric acid (PBA) forms chloropropanol phenylborate derivatives by alkylation which can be carried at a wide range of pH (strongly acidic to strongly basic pH) and in aqueous solutions but its derivatives are relatively unstable comparing to chloropropanol heptafluorobutrate derivatives.[14,25] The stability of phenylborate chloropropanol derivatives was kept for less than 36 hrs when tested stability of its derivatives (data not shown). The used derivatization reagent, HFBA, enables to volatile all co-eluted compound containing –OH and –NH groups thereby minimizing contamination of GC column. Moreover, the excess of HFBA would be conveniently removed by $H_2O$ washing.[16] Thereby HFBA was used to derivatize chloropropanols in this study based on its advantages over PBA.

### 3.2. Aanalytical method

The analytical conditions of apparatus to identify and quantify heptafluorobutyrate derivatives of 3-MCPD and 1,3-DCP were optimized as described above in apparatus conditions. Each chloropropanol standard and its isotope were used to set up analytical conditions for GC/MS. The chromatograms from the mixture of derivatized 3-MCPD and 1,3-DCP standard spiked with their isotopes were separated on none-polar (5% pused-Phenyl-methylpolysiloxane) GC capillary column (*Fig.* 2). There was no interference between peaks of targeted compounds as well as between peaks of targeted compounds and impurities. The targeted compounds were separated well in the order of 1,3-DCP-*d*5, 1,3-DCP, 3-MCPD-*d*5, and 3-MCPD. The spectra were analyzed by MS in EI mode at the full scan range of m/z 50-550. There was no interfence noticed in the presented study although others[16,18] reported that interferences found at m/z 253 for 3-MCPD. The characteristic ions resulted from fragmentation of 3-MCPD and 1,3-DCP derivatives were identical with fragment ions reported by Chung *et al.*[18] and Abu-El-Haj *et al.*[21] The major characteristic ions of each chloropropanol derivative were selected from each spectrum based on their relative response abundances to increase analytical sensitivity of measurements as described above (*Fig.* 3).

The analytical method was validated by determining the linearity, the limit of quantitation (LOQ), and recovery rate of chloropropanols (*Table* 3). The response of the calibration standards for both 3-MCPD and 1,3-DCP were found to be linear at a

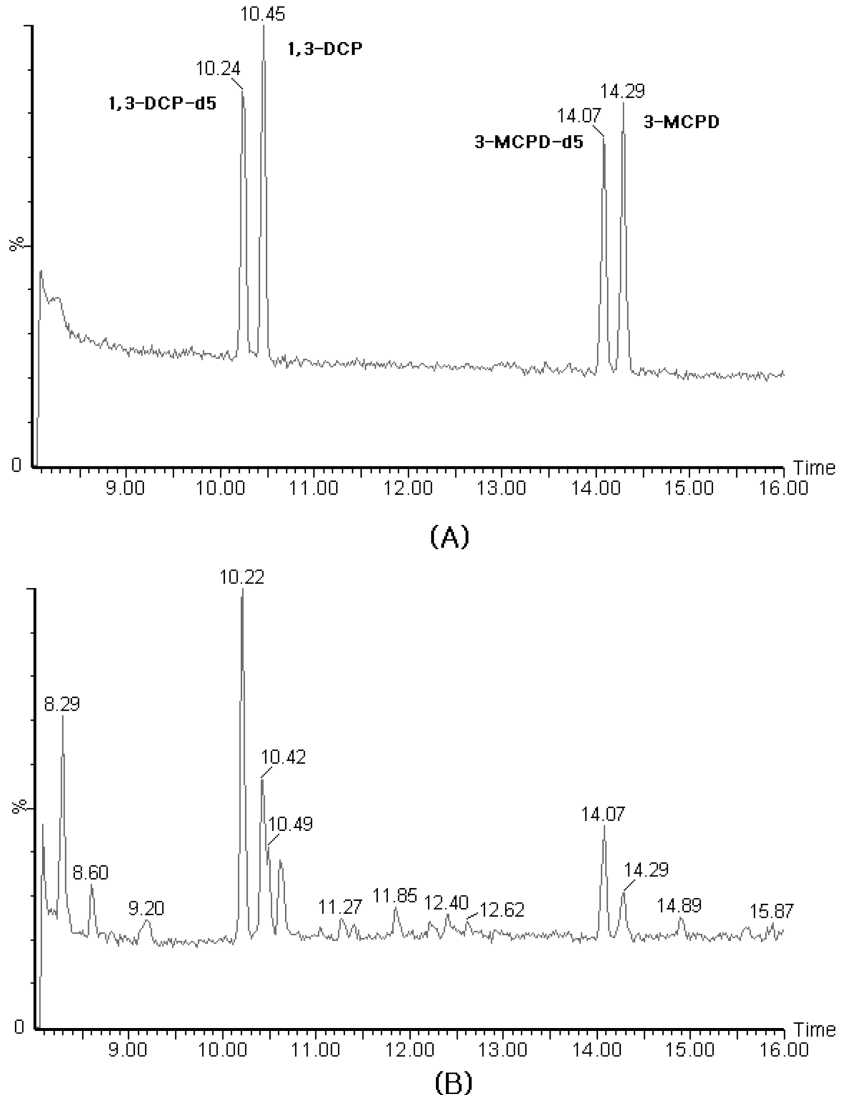


*Fig.* 2. The chromatograms from chloropropanol standards (A) and sauce sample (B).

concentration rage of 10~1000 ng/kg with correlation coefficients ($R^2$) of 0.999 or better. The LOQ of 3-MCPD and 1,3-DCP were determined by computing repeatable signal-to-noise ratio measured from blank sample (16% NaCl solution) spiked with each chloropropanol at 10 ng/kg. The signal-to-noise ratio of 10:1 was used to estimate the LOQ. The LOQ of both 3-MCPD and 1,3-DCP was 10 ng/kg. The recovery rate of 3-MCPD and 1,3-DCP were determined by analyzing various food (soy sauce, soup paste concentrate, and seasoning food powder) fortified with chcloropropanols at 50~400 ng/kg. The average recovery rates were 97.1% with 6.3% of RSD for 3-MCPD and 96.7% with 6.9% of RSD for 1,3-DCP.

### 3.3. Chloropropanols in food

The survey results of chloropropanols in various food items purchased from local grocery markets in Korea were summarized (*Table* 4). None of food tested was positive for 1,3-DCP contamination. Some food items were contaminated with 3-MCPD

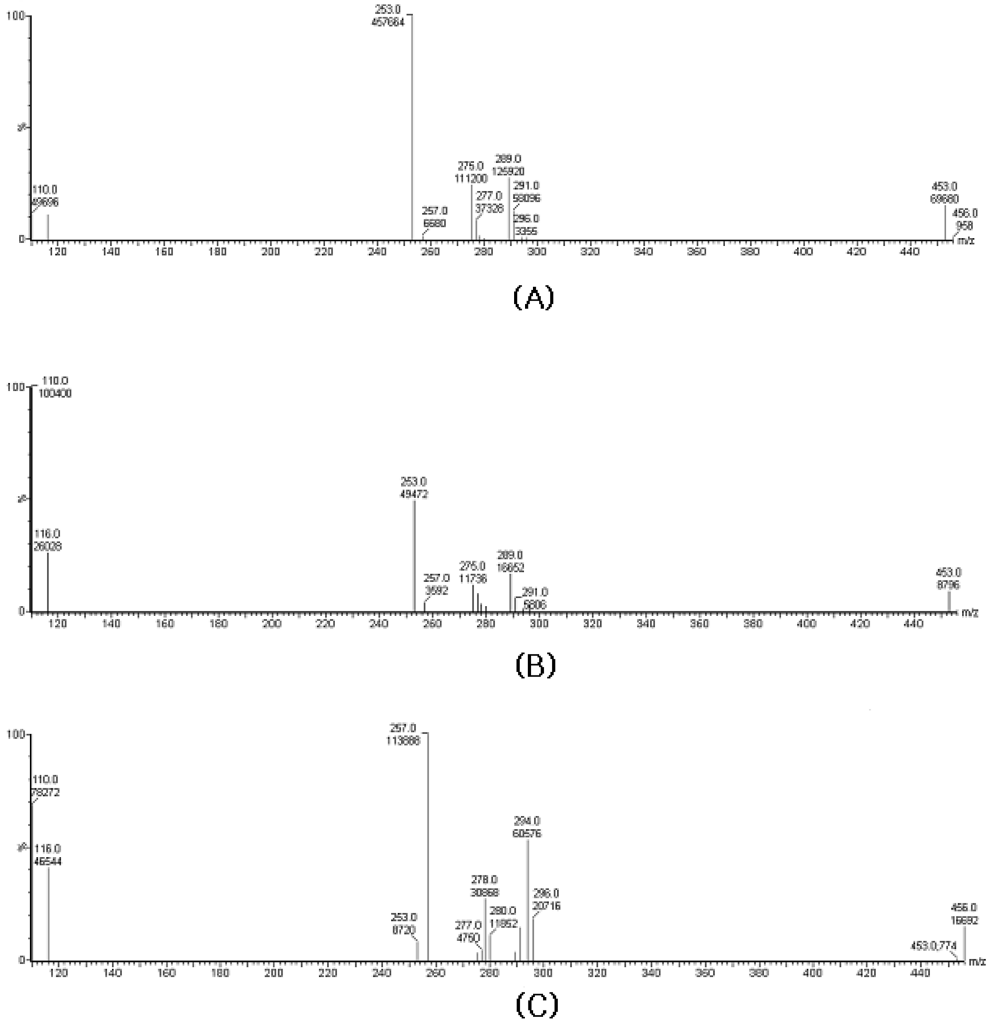


*Fig.* 3. The MS spectra from 3-MCPD standard (A), internal standard (B), and food sample (C).

*Table* 3. The validation results of the analytical method

| Validation factors | | 3-MCPD | 1,3-DCP |
|---|---|---|---|
| Linearity (mg/kg) | | 0.01~1.00 ($R^2$=0.999) | 0.01~1.00 ($R^2$=0.999) |
| Analytical limits (mg/kg) | LOD | 0.003 | 0.003 |
| | LOQ | 0.010 | 0.010 |
| Recovery (CV) (%) | Liquid[1)] | 104.0 (7.1) | 102.1 (6.9) |
| | Powder[2)] | 99.8 (6.4) | 96.8 (7.2) |
| | Paste[3)] | 87.5 (7.5) | 91.3 (6.8) |

[1)] Soy sauce n=9
[2)] Seasoning powder n=6
[3)] Soup concentrate, n=6

over concentration of 0.1 mg/kg but were not contaminated with 1,3-DCP. The presented results were agreed with the previous study. It reported that 1,3-DCP was only detected in food contaminated

*Table* 4. The detection levels of 3-MCPD and 1,3-DCP in various food items

| Category | Food item | No. | Positive No. | | Detected Range (mg/kg) | |
|---|---|---|---|---|---|---|
| | | | 3-MCPD | 1,3-DCP | 3-MCPD | 1,3-DCP |
| Seasoning | Sauce | 47 | 20 | 0 | 0.1~0.3 | - |
| | Soy sauce | 27 | 8 | 0 | 0.1~0.3 | - |
| | Curry powder | 10 | 3 | 0 | 0.0~0.2 | - |
| Processed meat | Sausage | 3 | 0 | 0 | - | - |
| | Ham | 8 | 4 | 0 | 0.1~0.2 | - |
| | Meat boiled[1)] | 2 | 0 | 0 | - | - |
| | Other meat | 1 | 0 | 0 | - | - |
| Fishery products | Fish sausage | 4 | 0 | 0 | - | - |
| | Others | 7 | 6 | 0 | 0.1~0.3 | - |
| Pickles | Vegetable | 2 | 2 | 0 | 0.1~0.2 | - |
| Others | Dried food | 16 | 8 | 0 | 0.0~0.1 | - |
| | Reay-to-eat meal | 15 | 5 | 0 | 0.1 | - |

[1)]The food samples were meat boiled down with soy sauce

with 3-MCPD at higher concentration and 1,3-DCP was undetectable or detected at significantly lower levels.[23] Detection of 3-MCPD should not result in contamination of 1,3-DCP although the more contamination of 3-MCPD was the more suspicious detection of 1,3-DCP.[20,26] However, 3-MCPD was found in various food items.

In general, detection of chloropropanols (3-MCPD or 1,3-DCP) were frequently found in soy sauces and sauces which contained HVP. In addition other food items containing soy protein in forms of fermented or acid-hydrolyzed were not free of 3-MCPD. The detection range of 3-MCPD in soy sauces (n=8/27) was 0.1~0.3 mg/kg. Most of soy sauces tested contained HVP (n=25/27) but few soy sauces tested were positive for 3-MCPD contamination. For sauces any other than soy sauce, 3-MCPD was detected at a range of 0.1~0.2 mg/kg (n=20/47). Among sauces tested some contained HVP (n=14), soy sauce (acid-HVP or mixed, n=8) or HVP with soy sauce (n=2). The 3-MCPD was detected in sauces containing either HVP or soy sauce and sauces containing concentrate of fishery extract. The 0.1~0.2 mg/kg of 3-MCPD was detected in curry powder tested (n=3/10). The detection of 3-MCPD was strongly related to presence of HVP in the tested curry powder. All curry powder containing HVP resulted in positive detection of 3-MCPD. The processed meat products (n=4/14) such as pressed ham, sausages, and other products were contaminated with 3-MCPD at a range of 0.1~0.2 mg/kg. Among meat products showing 3-MCPD positive the only one product contained vegetable protein which was not known to be produced by acid- hydrolysis or not. The fish sausages and fishery dishes were analyzed contamination of 3-MCPD. The results showed fishery products (n=6/11) were contaminated with 3-MCPD at the range of 0.1~0.3 mg/kg. The products contaminated with 3-MCPD contained soy sauce, soy sauce based condiments, or fermented soy protein powder. Other foods including soup paste concentrate, ready-to-eat entrée, powdered sauce, and pickled vegetables were determined contamination of 3-MCPD. Foods made of soy sauce, HVP, soy sauce powder, or fermented soy protein (n=15/33) resulted detection of 3-MCPD at a range of 0.1~0.2 mg/kg.

The UK reported that sauces and soy sauces (n=32/100) were 3-MCPD positive at a range of 0.0~93.1 mg/kg and 22 samples resulted over 0.3 mg/kg in 2000 while sauces including soy sauce (n=8/99) were 3-MCPD positive at a range of 0.0~21.2 mg/kg and only 4 samples were over 0.3 mg/kg of 3-MCPD in 2002.[27] The survey data

showed that soy sauces and sauces (n=58/157) were contaminated with 3-MCPD at a range of 0.0~0.8 mg/kg and 0.0~0.4 mg/kg, respectively in 2002 in Korea.[28] These levels of 3-MCPD were higher than those in 2007. The safety concern for 3-MCPD would be not necessary based on the survey results from the present study where no food item was contaminated over the standard of 3-MCPD (0.3 mg/kg) in Korean Food Code. Although the levels of 3-MCPD contamination decreased recently the more effort would be made to reduce 3-MCPD as well as 1,3-DCP. Thereby there is no faced problem to export soy sauces and other product containing soy sauce to Europe where the standard for 3-MCPD in soy sauce is set at 0.02 mg/kg as liquid based.

## 4. Conclusion

The developed method for the determination of chloropropanols, 3-MCPD as well as 1,3-DCP resulted in fairy good validation properties and was satisfactory for the application in determination of chloropropanols in various food. The survey data showed that the detected level of 3-MCDP in foods was lower than that of standard in Food code.

## References


1. J. Valisek, K. Davidek, V. Kubelka, Z. Janicek, Z. Svobodova and Z. J. Simikova, *Agric. Food Chem*. **28**, 1142-1144(1980).
2. P. Collier, D. Cromie and A. J. *Davies, Am. Oil Chem. Soc*. **68**, 785-790(1991).
3. Food Standard Agency. Surveillance Information Sheet, No. 181 (1991).
4. Food Standard Agency. Surveillance Information Sheet, No. 187 (1991).
5. Food Standard Agency. Surveillance Information Sheet, No. 14/01 (2001).
6. Food Standard Agency. Surveillance Information Sheet, No. 15/01 (2001).
7. European Commision Directorate-General Health and Consumer Protection. http://europa.eu.int/comm/food/food/chemicalsafety/contaminants/mcpd_en.htm
8. C. Crews, P. Hough, P. Brereton, D. Harvey, R. MacArthur and W. Matthews, Food Additi. Contamin. **19**, 22-27(2002).
9. JECFA (Joint FAO/WHO Expert Committee on Food Additives) Prepared by the 57th meeting of the JECFA. WHO *Food additives series*, No. 48. WHO, Geneva, 401-432 (2002).
10. COC (Committee on Carcinogenicity of Chemicals in Food. Statement, COC/01/S1, January (2001).
11. B. Lynch, D. Bryant, G. Hook, E. Nestmann and I. Munro, *International Journal of Toxicology,* **17**, 47-76 (1998).
12. S. Robjohns, R. Marshall, M. Fellows and G. Kowalczyk, *Mutagenesis,* **18**, 401-404(2003).
13. G. J. Spyres, *Chromatogr. A*. **638**, 71-74(1993).
14. W. J. Plantinga, W. G. Van Toorn and G. H. D. J. Stegen, *Chromatogr. A*. **555**, 311-314(1991).
15. E. J. Kissa, *Chromatogr*. **605**, 134-138(1992).
16. C. Hamlet, *Food Addti. Contam.* **15**, 451-465(1998).
17. D. Meierhans, S. Bruehlmann, J. Meili and C. Taeschler, *J. Chromatogr. A*. **802**, 325-333 1998).
18. W. Chung, K. Hui and S. Cheng, *J. Chrom. A*., **952**, 185-192(2002)
19. P. Brereton, J. Kelly, C. Crews, S. Honour and R. J. Wood, AOAC *Intl*., **84**, 455-465(2001).
20. C. Crews, G. LeBrun and P. Brereton, *Food Additives and Contaminants*, **19**, 343-349(2002).
21. S. Abu-El-Haj, M. Bogusz, Z. Ibrahim, H. Hassan and M. Tufail, *Food control*, **18**, 81-90(2007).
22. K. Ushuima, Y. Deguchi, K. Kikukawa, T. Nomura and T. Adach, *Shokushin Eiseigaku Zasshi,* **36**, 360-364 (1995).
23. P. Nyman, G. Diachenko and G. Perfetti, *Food Additiv., Contamin.* **20**, 903-905(2003).
24. C. Crew, P. Brereton and A. Davies, *Food Additiv. Contamin.* **18**, 271-280(2001).
25. L. E. Rodman and R. D. Ross, *J. Chromatogr. A*. **69**, 97-103(1986).
26. P. Nyman, G. Diachenko and G. Perfetti, *Food Additiv. Contamin.* 10, 909-915(2003).
27. C. Crew, S. Hasnip, S. Chapman, P. Hough, N. Potter, J. Todd, P. Brereton and W. Matthews, *Food Additv. Contamin.* **20**, 916-922(2003).
28. H Lee and C. Oh, *The annual report of National Institute of Toxicological Research* **1**, 265-312(2002).