Sensitive method for the determination of 1,3-dichloropropan-2-ol and 3-chloropropane-1,2-diol in soy sauce by capillary gas chromatography with mass spectrometric detection

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Abstract

This paper reports the development of a highly selective and sensitive method for the determination of parts-per-billion level of 1,3-dichloropropan-2-ol (1,3-DCP) and 3-chloropropane-1,2-diol (3-MCPD) in soy sauce using capillary gas chromatography with mass spectrometric detection. Samples were homogenised, mixed with sodium chloride solution and then adsorbed on silica gel. The loaded silica gel was packed into a chromatographic column, from which chloropropanols were extracted by elution with ethyl acetate. Heptafluorobutyric acid anhydride was added to the concentrated eluant to derivatise the chloropropanols and the derivatised analytes were separated by gas chromatography, identified and quantified by mass spectrometry. A linear relationship between the concentration of the two chloropropanols and the detector response was obtained over the concentration range of 10–1000 µg/kg. Precision of the method was satisfactory at about 5%, and recoveries of 1,3-DCP and 3-MCPD from soy sauce samples spiked at 25 µg/kg were 77 and 98%, respectively. The limit of quantitation of the method was found to be about 5 µg/kg for 1,3-DCP and 3-MCPD, respectively meeting the requirements of tolerance limits adopted by different international institutions and governments around the world. This paper is the first of its kind in reporting an analytical procedure for the simultaneous separation and determination of 3-MCPD and 1,3-DCP, a more potent contaminant, at low µg/kg level.   © 2002 Published by Elsevier Science B.V.

Keywords: Soy sauce; 1,3-Dichloropropan-2-ol; 3-Chloropropane-1,2-diol; Chloropropanols

1. Introduction

Acid Hydrolyzed Vegetable Protein (acid-HVP) is a widely used ingredient of savoury foods such as soups, prepared meals, savoury snacks, gravy mixes and stock cubes. It is produced by acid hydrolysis of plant protein-containing raw materials, such as wheat and rice gluten and roughly ground soybeans, palm kernels or peanuts. Hydrolysis of HVP normally proceeds at temperatures above 100 °C and at appropriate pressure in the presence of hydrochloric acid. Residual fatty acid esters (glycerol) present in the raw material will also undergo hydrolysis forming chloropropanols [1,2]. Amongst others, 1,3-dichloropropan-2-ol (1,3-DCP) and 3-chloropropane-1,2-diol (3-MCPD) are two of the most toxic chloropropanols found as contaminants in acid-hydrolysed vegetable protein (acid-HVP) [3–5], and a range of

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other foods and ingredients, most notably in soy sauce [6,7].

Based on the findings of a toxicological review, the European Commission's Scientific Committee for Food concluded that 3-MCPD should be regarded as a genotoxic carcinogen in 1995 [8]. In 1996, the review was further endorsed by the United Kingdom's Food Advisory Committee that advocated to have levels of 3-MCPD in all foods and ingredients reduced to the minimum detectable by the most sensitive method available [5]. Reports on the excessive concentration of 3-MCPD in soy sauce and related products were made public in mid-1999 [6,9]. As a result, several different brands of soy and related sauces that were found to contain 3-MCPD exceeding the British recommended limit of 0.01 mg/kg were taken out of grocery stores in Britain. Similar tests carried out in Canada in the same period on soy sauces imported from the People's Republic of China (PRC) were found to contain 3-MCPD at levels ranging from below 0.01 to 177.5 mg/kg [10]. The two latest surveys of 3-MCPD and 1,3-DCP levels in food ingredients conducted by the Ministry of Agriculture, Food and Fisheries, UK reported on the results of 100 samples of soy sauce that were on sale in the British market during August 2000 [11,12]; 22% of samples analysed were found to contain levels of 3-MCPD [11] above the EC limit of 0.02 mg/kg whilst 17% of samples were found to contain quantifiable levels of 1,3-DCP, the quantification limit of which was stated to be 0.005 mg/kg [12]. All samples found to contain 1,3-DCP were also found to contain 3-MCPD at concentrations greater than 0.02 mg/kg.

The latest assessment of the toxicity of 3-MCPD conducted in the UK concluded that 3-MCPD can be regarded as having no significant genotoxic potential in vivo, but has observable carcinogenic effects in animals [13,14]. On the other hand, while not tested in vivo, 1,3-DCP has been found to be mutagenic in bacterial and mammalian cell systems in vitro [15]. One carcinogenicity study has been reported, with 1,3-DCP administered in drinking water to rats and positive results obtained. However, much of the data are not available in the public domain [15]. On the basis of these limited information, it is safe to regard 1,3-DCP as a genotoxic carcinogen [15]. Based on technological feasibility and a preliminary quantita-

tive cancer risk assessment by the Food and Drug Administration of United States, specifications of 1 mg/kg 3-MCPD and 0.05 mg/kg 1,3-DCP in acid-hydrolysed vegetable proteins (on dry basis) were established by the Food Chemicals Codex in December 1997 [16].

The European Community has agreed that a limit of 0.02 mg/kg for 3-MCPD in acid-HVP and soy sauce is to be implemented in April 2002 [16]. In September 2001, the People's Republic of China adopted its national standard ''GB 1818–2000'' that stipulates a limit of 0.01 mg/kg for 3-MCPD in soy sauce and related products.

In the literature, very limited information is available for the simultaneous separation and determination of 1,3-DCP and 3-MCPD at low µg/kg levels. Gas chromatography with different detectors was shown to be the method of choice for the quantitation of the two chloropropanols under study. Most of these earlier methods relied on the detection of either the underivatised 3-MCPD [17] or the derivatives of 3-MCPD with phenylboronic acid [18–21] and butaneboronic acid [22], and the derivatives of the chloropropanols with N,O-bis-(trimethylsilyl)trifluoroacetamide [23]. Determination of 10–100 µg/kg level of 1,3-DCP has also been reported [24–27], however the detection limits of 3-MCPD for these methods, if so reported, are in the ranges of 50–100 µg/kg. In sum, none of these methods are of sufficient sensitivity or selectivity for the simultaneous determination of low µg/kg levels of 3-MCPD and 1,3-DCP in foodstuffs.

In 1997, Hamlet et al. [28,29] reported an analytical method for the determination of 3-MCPD and 2-chloropropane-1,3-diol (2-MCPD) at µg/kg levels in HVP, seasonings and food products using gas chromatography/ion trap tandem mass spectrometry. In the following year, Meierhans et al. [30] developed an alternative gas chromatographic/mass spectrometric (GC–MS) method for the determination of 3-MCPD and 2-MCPD. However, hitherto, no analytical method for the simultaneous separation and quantitation of 3-MCPD and 1,3-DCP, a more potent contaminant, at concentrations about the current action limits adopted by the international communities is available in the literature. To this end, the aim of this study is to develop an efficient and sensitive analytical protocol that would provide

valid analytical measurement in meeting the new action limits for 1,3-DCP and 3-MCPD in soy sauce and related products.

2. Materials and methods

2.1. Chemicals and reagents

1,3-DCP and 3-MCPD were purchased from BDH. An alternative source of 3-MCPD was acquired from Sigma for cross checking. d_5-3-Monochloro-1,2-propanediol (d_5-3-MCPD) was purchased from Brunschwig Chemie B.V., Netherlands. All standards were of purity of over 99.0%. Heptafluorobutyric acid anhydride (Lancaster, UK), ethyl acetate, isooctane and sodium sulphate were obtained commercially. Ethyl acetate and isooctane were re-distilled before use. All other chemicals and solvents were of analytical reagent-grade and were used without further purification. Ultrapure water was supplied by a Milli-Q UV plus system to a purity of <17 MΩ/cm from Millipore (Bedford, MA, USA).

2.2. Preparation of standards

Stock standard solutions of 1,3-DCP, 3-MCPD and d_5-3-MCPD were prepared at concentration of 1 mg/ml in ethyl acetate by dissolution of the neat chemicals in quantitative amounts of solvent. d_5-3-MCPD was used as the internal standard.

Mixed working standard solutions were prepared for calibration by mixing a quantitative amount of each of the stock standard solutions and diluting the mixture with ethyl acetate to give concentrations of the chloropropanols in the range of 0.02–1.0 μg/ml with the internal standard at 1.0 μg/ml.

A mixed spiking standard solution of 1,3-DCP and 3-MCPD at 2 μg/ml each was prepared similarly by serial dilution of the respective stock standard solutions with ethyl acetate. A spiking internal standard solution of 10 μg/ml was also prepared by serial dilution of the stock d_5-3-MCPD with ethyl acetate.

2.3. Gas chromatography–mass spectrometry-selected ion monitoring (GC–MS-SIM)

Capillary GC–MS-SIM analysis was carried out on a Hewlett-Packard 6890 gas chromatograph equipped with a Series 5973 mass selective detector, a Series 7673A automatic sampler and a data processing system (Hewlett-Packard, Avondale, PA). Gas chromatography was performed on a DB-5MS fused-silica capillary column (30 m, 0.25 mm I.D., 0.25 μm film thickness; Hewlett-Packard, Avondale, PA). Ultra-high-purity helium was used as the carried gas at constant flow of 0.9 ml/min.

A split-splitless injection system operating in the splitless mode with quartz 2 mm I.D., 250 μl, deactivated splitless injector liner was employed. One minute after the injection, the septum purge was activated to a flow-rate of 23 ml/min for 1 min. Afterwards, the total flow was set to 20 ml/min. The initial column temperature was set at 50 °C. After the sample injection, it was increased at 2 °C/min to 90 °C, maintained for 5 min, then increased at 30 °C/min to 280 °C. The temperature of the injector was 250 °C. The mass spectrometer was operated in the electron-impact mode at 70 eV and the ion source temperature was set at 280 °C.

Qualitative and quantitative analysis was carried out by selectively monitoring the detector response of characteristic molecular ions ($[M]^{+\cdot}$) at m/z 110, 111, 112, 197, 275, 277 for the heptafluorobutyryl derivative of 1,3-DCP, at m/z 253, 275, 289, 291, 453 for the heptafluorobutyryl derivative of 3-MCPD and at m/z 257 for the heptafluorobutyryl derivative of d_5-3-MCPD. The dwell time for monitoring each m/z is 50 ms.

2.4. Sample preparation

2.4.1. Sample extraction

About 8 g of a homogenised sample was weighed and placed into a 200 ml-beaker; 500 μl of the spiking internal standard solution was added into the sample; 10 ml of 5 M sodium chloride solution was added to the mixture which was then stirred to a homogeneous mixture with the aid of a spatula. The mixture was sonicated in an ultrasonic bath for 10 min at room temperature.

A 15-g aliquot of silica gel (60 mesh) was added to the sample. The mixture was mixed thoroughly by stirring and crushing with a spatula. The reconstituted mixture was totally transferred to a chromatographic glass column (3 cm I.D., 100 cm length).

The column was gently shaken or vibrated to compact the contents. A 1-cm layer of anhydrous sodium sulphate was placed on top of the column packing; 150 ml of ethyl acetate was used to elute the column at a flow-rate of about 8 ml/min. The eluate was filtered through anhydrous sodium sulphate into a 250 ml round-bottomed or pear-shaped flask.

The eluate was concentrated to about 5 ml by rotary evaporation at 35 °C. The concentrated extract was totally transferred to a 10-ml volumetric flask. Ethyl acetate was then added to make up the volume to the mark. A small quantity (about 10–50 mg) of sodium sulphate was added to the flask, which was then shaken and left stand for a brief period of 5–10 min.

2.4.2. Derivatisation

A 2-ml aliquot of the sample extract as obtained above was transferred into a test-tube and evaporated to about 0.2 ml at room temperature under a gentle stream of nitrogen. Drying of the eluate at this stage was also found to result in significant loss in recovery of the 1,3-DCP; 200 μl of heptafluoro-butyric acid anhydride (HFBA) was added to the concentrated sample extract. The mixture was shaken with a Vortex mixer for 1 min and was left at room temperature for 2 h. After that, 1 ml of isooctane and 5 ml of distilled water were added. The mixture was allowed to separate into two phases after shaking with a vortex mixer for 30 s. The shaking process was repeated one more time. The organic phase was then removed and transferred to another clean test-tube containing a small quantity of anhydrous sodium sulphate in the bottom. Shortly afterwards, the derivatised extract was transferred to a clean 2-ml vial. A 2-μl aliquot of the extract was injected into the GC–MS for analysis.

2.5. Calibration graphs

One milliliter of mixed calibration standards, containing 0.02, 0.05, 0.1, 0.5 and 1.0 μg/ml of 1,3-DCP and 3-MCPD and 1.0 μg/ml of internal standard were concentrated to about 0.2 ml at room temperature under a gentle stream of nitrogen. The standards were derivatised according to the same procedures as described for the sample. A 2-μl aliquot of each of the standard solutions was injected

into the GC–MS and the retention times and peak areas of 1,3-DCP, 3-MCPD and d_5-3-MCPD were recorded. The peak-area ratios of analyte against internal standard (m/z 275–257 for 1,3-DCP and m/z 289–257 for 3-MCPD) were determined. Two five-point calibration graphs were obtained by plotting the respective peak-area ratios (y-axis) against the concentrations of 1,3-DCP and 3-MCPD (x-axis) using unweighted least-squares linear fitting.

3. Results and discussion

3.1. Chromatography of HFBA derivatives

Despite the fact that HFBA is a common derivatisation agent used for characterization of alcohols in gas chromatographic analysis, this study is the first to report the use of HFBA as the derivatisation agent for the measurement of 1,3-DCP and 3-MCPD. HFBA was found to react selectivity with both the isotopic internal standard and the chloropropanols under study giving stable hepta-fluorobutyrate derivatives (Fig. 1) that were found to undergo fragmentation into characteristic ions for characterization and quantitation of the chloro-propanols upon electron impact.

The full scan EI mass spectra of 1,3-DCP, 3-MCPD and d_5-3-MCPD made over the mass range m/z 50–550 at 1 s/scan are shown in Fig. 2a–c. Apart from some major ions derived from the heptafluorobutyryl moiety such as m/z 69, 100, 119 and 169, the EI spectra of the heptafluorobutyrate derivatives 1,3-DCP and 3-MCPD exhibit a number of characteristic ions (Table 4). Though these
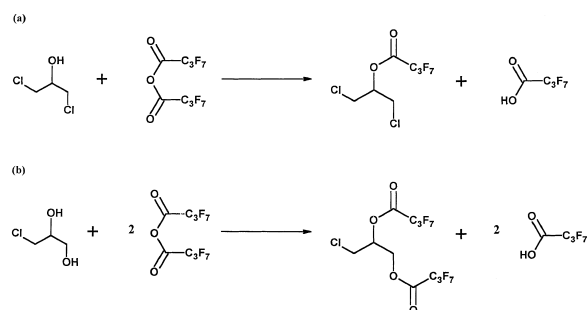

Fig. 1. (a) Reaction of 1,3-DCP with HFBA and (b) reaction of 3-MCPD with HFBA.
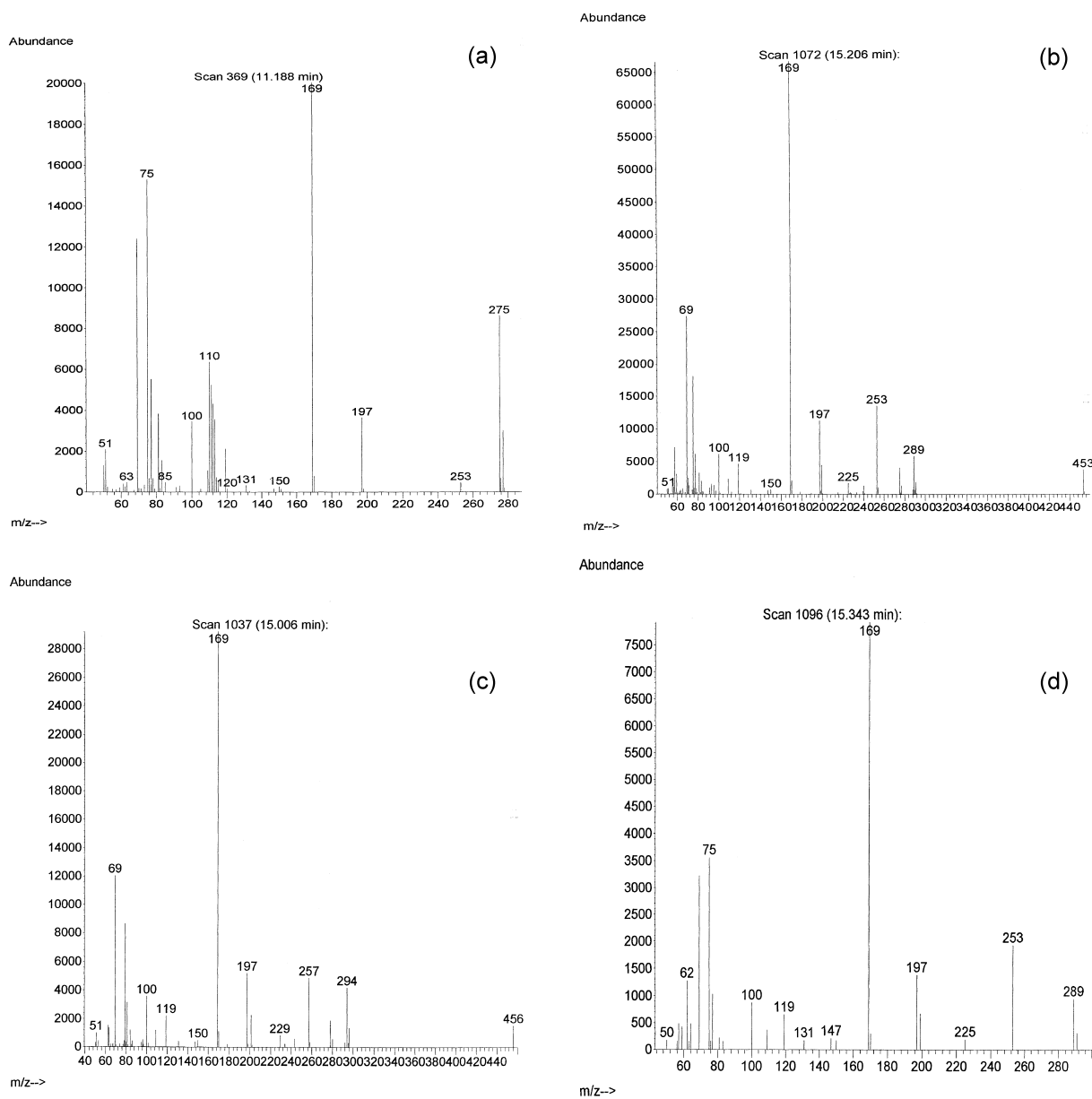
Fig. 2. (a) Mass spectrum of HFBA derivatised 1,3-DCP. (b) Mass spectrum of HFBA derivatised 3-MCPD. (c) Mass spectrum of HFBA derivatised d_5-3-MCPD. (d) Mass spectrum of HFBA derivatised 2-MCPD.

characteristic ions are less intense than the ions deriving from the heptafluorobutyryl moiety, they provide evidence to support the equivocal assignment and confirmation of the presence of the chloropropanols.

To enhance the sensitivity of measurement, selective ion monitoring was used to monitor characteristic ions at m/z 110, 111, 112, 197, **275**, 277 (1,3-DCP), m/z 253, 275, **289**, 291, 453 (3-MCPD) and m/z **257** (d_5-3-MCPD). Co-eluted interference was found in sample spectra at m/z 110, 111, 112, 197 for 1,3-DCP, and at m/z 253, 275 for 3-MCPD.

Table 1
Recovery of 1,3-DCP from blank samples spiked at 25 μg/kg level

Matrix	Spiked level (μg/kg)	n	Mean recovery (%)	RSD (%)
Soy sauce	25	3	76.7	4.1
Oyster sauce	25	3	48.6	6.1

Table 2
Recovery of 3-MCPD from blank samples spiked at 25 μg/kg level

Matrix	Spiked level (μg/kg)	n	Mean recovery (%)	RSD (%)
Soy sauce	25	3	104	0.8
Oyster sauce	25	3	108	0.6

Table 3
Analysis of 1,3-DCP and 3-MCPD in matrix blanks fortified at 5 μg/kg level

Analyte	n	Mean recovery (%)	SD	CV (%)
1,3-DCP	5	98	0.19	3.8
3-MCPD	5	120	0.22	4.4

Hamlet et al. [18] also reported the interference of co-extracted materials at m/z 253 for the determination of 3-MCPD. To this end, the characteristic peak area ratios of the ions at m/z 275–277 for 1,3-DCP and at m/z 289–291 for 3-MCPD were used as part of the acceptance criteria for confirmation of the presence of the two chloropropanols. The ratios were found to be 3 ± 0.45 for all valid standard and sample injections. Identification of 1,3-DCP and 3-MCPD was also verified by matching the retention time and relative retention time of the two analytes in samples against those in standards. The retention time of 1,3-DCP, 3-MCPD and the internal standard

were to lie within ±0.2 min of the mean of those of the calibration standards. The relative retention time of 1,3-DCP and 3-MCPD to d_5-3-MCPD were found to be within $\pm0.5\%$ of the mean of those of the calibration standards.

The concentrations of 1,3-DCP and 3-MCPD were calculated based on the relative peak area response of the characteristic ions of the analytes (m/z at 275 and 289 for 1,3-DCP and 3-MCPD, respectively) to that of the internal standard (m/z at 257).

3.2. Method validation

The responses of the calibration standards for both 1,3-DCP and 3-MCPD were found to be linear for the concentration range 0.01–1.0 μg/ml with correlation coefficients (r) of 0.999 or better. The homoscedasticity of the data was tested by applying Bartlett's variance test. The χ^2-value (for $P=0.05$, df 4) found for 1,3-DCP and 3-MCPD was 3.8 and 3.7, respectively indicating homogeneity among variance. Hence, the null hypothesis is accepted. At 95% confidence limits, the slope and intercept for the liner relationships between the respective peak-area ratios and the concentrations of the two analytes over the calibrated ranges are $(5.44\pm0.06)\times10^{-4}$ and $(-1.76\pm2.92)\times10^{-3}$ for 3-MCPD; and $(5.82\pm0.19)\times10^{-4}$ and $(-5.36\pm4.45)\times10^{-3}$ for 1,3-DCP, respectively. The retention time and relative retention time of the analytes in all valid injections were found to comply with the quality assurance requirements as specified above, demonstrating the stability of GC–MS system during the course of analysis.

The limit of quantitation (LOQ) was determined by repeatedly analysing matrix blank (16% (w/w) sodium chloride solution) fortified at 5 μg/kg for 3-MCPD and 1,3-DCP. The background response

Table 4
Characteristic ions in the EI mass spectra of the HFBA derivatives of 3-MCPD, 2-MCPD, 1,3-DCP and d_5-3-MCPD

Compound	MW	$[M\text{-}CH_2Cl]^+$	$[M\text{-}OC_3H_5Cl_2]^+$	$[M\text{-}C_3F_7CO_2]^+$	$[M\text{-}C_3F_7CO_2CH_2]^+$	$[M\text{-}C_3F_7CO_2\text{-}HCl]^+$	$[M\text{-}C_3F_7CO_2\text{-}CH_2Cl]^+$	$[M\text{-}C_3F_7CO_2\text{-}C_3F_7CO_2H]^+$
3-MCPD	502	453	–	289/291	275/277	253	240	75/77
2-MCPD	502	–	–	289/291	–	253	–	75/77
1,3-DCP	325	275/277	197	110/112	–	75/77	–	–
3-MCPD-d_5	507	456	–	294/296	278/280	257	243	79/81

and standard deviation are computed (Table 3). At LOQ, the variation and bias for both analytes were less than 5% and less than 20%, respectively. The levels of 1,3-DCP and 3-MCPD in reagent blanks, matrix blanks and sample blanks were found to be below the limit of detection.

The derivatisation process was found to affect critically the recovery of 1,3-DCP, but not 3-MCPD. Shortening of the reaction time from 2 to 1 h or lowering the amount of derivatisation agent from 200 to 100 μl would reduce recovery of 1,3-DCP significantly. Amongst these different conditions, 200 μl HFBA and 2 h derivatisation time provide best recovery for 1,3-DCP.

To estimate the recovery and precision of the method, blank soy and oyster sauce samples spiked at 25 μg/kg for both analytes were analysed. Tables 1 and 2 show that the average recoveries of 1,3-DCP and 3-MCPD in spiked soy sauce samples were 76.7 and 104.1%, respectively with a corresponding RSD of 4.1 and 0.8%. Similarly, the average recoveries of 1,3-DCP and 3-MCPD in oyster sauce spiked at 25 μg/kg were found to be 48.6 and 107.7% with a RSD of 6.1 and 2.1%, respectively (Tables 1 and 2).

Samples containing high levels of 3-MCPD were also found to contain 2-MCPD, an isomer of 3-MCPD. The presence of 2-MCPD was confirmed by the characteristic ions at m/z at 253, 289 and 291 (Fig. 3). Such findings were in line with those reported earlier by Hamlet [23]. Nevertheless, quantitation of 2-MCPD was not carried out in the present study owing to the absence of a commercially available standard of 2-MCPD. The full scan EI mass spectra of 2-MCPD made over the mass range m/z 50–550 at 1 s/scan is shown in Fig. 2d.

4. Conclusions

This paper is the first of its kind to report the simultaneous determination of 1,3-DCP and 3-MCPD in soy sauce at low μg/kg level using a GC–MS technique. The analytical protocol is described and verified to give satisfactory recovery of over 70% and precision of less than 10% for measurement of 1,3-DCP and 3-MCPD at low μg/kg range in soy sauce. Satisfactory recovery of 3-MCPD was also recorded when the analytical procedures were extended to the analysis of oyster sauce, although the recovery of 1,3-DCP in the same matrix was lower at about 50%.

In conclusion, the method, by not requiring too tedious and complicated analytical procedures, enables a satisfactory turn-round time of about 1 day for a batch of 10–15 samples, to be achieved by experienced analysts, thus providing an efficient and robust means for the determination of the two chloropropanols in soy sauce. The use of simple laboratory glassware in the purification of samples and commonly used bench-top GC–MS in analysis also makes the method suitable for routine determination of the two chloropropanols at reasonable running costs.
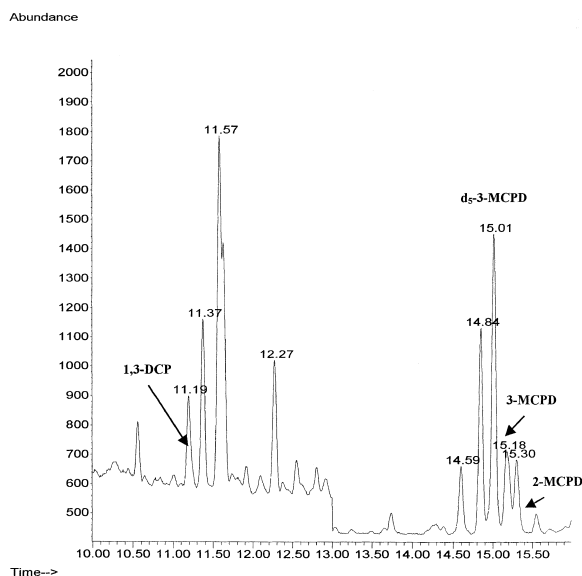
Fig. 3. Total ion current chromatogram of HFBA derivatised chloropropanols in soy sauce.

References

[1] J. Velisek, K. Davidek, V. Kubelka, Z. Janicek, Z. Svobodova, Z. Simikova, J. Agric. Food Chem. 28 (1980) 1142.
[2] P.D. Collier, D.D.O. Cromie, A.P. Davies, J. Am. Oil Chem. Soc. 68 (1991) 785.
[3] Ministry of Agriculture, Fisheries and Food, Survey of hydrolysed vegetable proteins for chlorinated propanols, CSL Report FD 91/6, 1991.
[4] Ministry of Agriculture, Fisheries and Food, Survey of chlorinated propanols in hydrolysed vegetable protein 1992, CSL Report FD 93/117, 1993.
[5] Food Standards Agency, Survey of 3-monochloropropane-1,2-diol (3-MCPD) in acid-hydrolysed vegetable products, Food Surveillance Information Sheet, number 181, 1999.
[6] Food Standards Agency, Survey of 3-monochloropropane-1,2-diol (3-MCPD) in soy sauce and similar products, Food Surveillance Information Sheet, number 187, 1999.
[7] C. Crews, G. LeBrun, P. Hough, D. Harvey, P. Brereton, Czech. J. Food Sci. 18 (2000) 276.
[8] EC Scientific Committee for Food, Opinion on 3-Monochloropropane-1,2-diol (3MCPD) (expressed on 16 December 1994), Annex 4 to document III/5488/94, CS/CNTM/OTH/2 Final, 1995.
[9] UK Food Advisory Committee, Press Releases FAC 6/96 (19 June 1996) and FAC 13/96 (7 November 1996), Update on Chloropropanols in Hydrolysed Vegetable Protein, 1996.
[10] World Food Chemical News, December 22, 1999.
[11] Food Standards Agency, Survey of 3-monochloropropane-1,2-diol (3-MCPD) in soy sauce and related products, Food Surveillance Information Sheet, number 14/01, 2001.
[12] Food Standards Agency, Fisheries and Food, Survey of 1,3-dichloropropanol (1,3-DCP) in soy sauce and related products, Food Surveillance Information Sheet, number 15/01, 2001.
[13] Committee on Mutagenicity of Chemicals in Food, Consumer Products and the Environment, Statement on mutagenicity of 3-monochloropropane-1,2-diol (3-MCPD), 2000. Statement available at http://www.doh.gov.uk/mcpd2.htm
[14] Committee on Mutagenicity of Chemicals in Food, Consumer Products and the Environment, Statement on carcinogenicity of 3-monochloropropane-1,2-diol (3-MCPD), 2000. Statement available at http://www.doh.gov.uk/mcpd1.htm
[15] TNO BIBRA, Toxicity Profile: 1,3-dichloro-2-propanol, TNO-BIBRA International Ltd, Carshalton, Surrey, UK, 1999.
[16] Position Paper on Chloropropanols for the thirty-third Session of the Codex Committee on Food Additives and Contaminants, Joint FAO/WHO Food Standards Programme, 2001.
[17] G. Spyres, J. Chromatogr. 638 (1993) 71.
[18] L.E. Rodman, R.D. Ross, J. Chromatogr. 369 (1986) 97.
[19] C.F. Poole, S. Singhawangcha, A. Zlatkis, J. Chromatogr. 158 (1978) 33.
[20] W.J. Plantingua, W.G. van Toorn, G.H.D. van der Stegen, J. Chromatogr. 555 (1991) 311.
[21] K. Ushijima, Y. Deguchi, K. Kikukawa, A.T. Nomur, T. Adachi, J. Food Hyg. Soc. Jpn. 36 (1995) 360.
[22] R.L. Pesselman, M.J. Feit, J. Chromatogr. 439 (1988) 448.
[23] I. Kissa, J. Chromatogr. 605 (1992) 134.
[24] W. van Rillaer, H. Beernaert, Z. Lebens. Unters. Forsch. 188 (1989) 343.
[25] R. Willmann, Z. Lebens. Unters. Forsch. 193 (1991) 224.
[26] C.A. van Bergen, P.D. Collier, D.D.O. Cromie, R.A. Lucas, H.D. Preston, D.J. Sissons, J. Chromatogr. 589 (1992) 109.
[27] D.S. Hu, Fenxi Kexue Xuebao 15 (1999) 522.
[28] C.G. Hamlet, P.G. Sutton, Rapid Commun. Mass Spectrom. 11 (1997) 1417.
[29] C.G. Hamlet, Food Addit. Contam. 15 (1998) 451.
[30] D.C. Meierhans, J. Bruehlmann, J. Meili, C. Taeschler, J. Chromatogr. A 802 (1998) 325.