GC/MS Approaches to the Analysis of Monochloropropanediol

Application

Foods and Flavors

Author

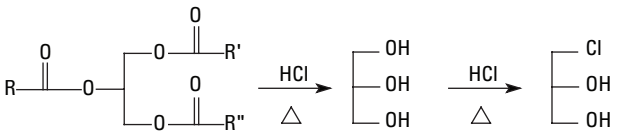
Harry Prest
Agilent Technologies, Inc.
1601 California Avenue
Palo Alto, California 94301-1111
USA

Abstract

The suspected carcinogen 3-chloro-1,2-propanediol (3-MCPD) is found in hydrolyzed vegetable protein, a widely used flavoring. Gas chromatography with mass spectrometric detection is a standard AOAC method. Electron impact ionization permits subpicogram measurement. Electron capture negative ionization is more selective and probably better suited to actual samples, with sensitivity of a few picograms in scan mode and less than 1 picogram in the selected ion mode.

Introduction

Hydrolyzed vegetable protein (HVP) is a widely used flavoring found in soups, sauces, and some meat products, etc. HVP is traded internationally both as solid and liquid depending upon the intended application. During the acid hydrolysis process of vegetable proteins, the hydrochloric acid agent reacts with triglycerides (Equation 1) to produce 3-chloro-1,2-propanediol (3-MCPD). This monochloropropanediol byproduct was classified by the European Union's Scientific Committee for Food as a suspected carcinogen [1].



Equation 1. The acid hydrolysis of vegetable matter from triglycerides to glycerol, and then to 3-MCPD.

Although efforts were made to reduce the presence of 3-MCPD, continuing concerns about its presence lead to regulation of the allowable concentration. Recently the Association of Official Analytical Chemists (AOAC) has published a method for the extraction, separation and identification of 3-MCPD in foods and ingredients using gas chromatography with mass spectrometric detection [2]. In brief, a homogenized sample is mixed with a salt solution, then mixed with an Extrelut™ refill pack before being added to chromatographic column. The 3-MCPD is eluted with diethyl ether and a portion is derivatized with heptafluorobutyrylimidazole. Quantitation with GC-MS using electron impact ionization provides detection limits less than 0.01 mg/kg (which is equivalent to about 10 pg/µL in the final extract at injection).

This brief examines approaches to 3-MCPD as the heptafluorobutyryl-derivative described in the AOAC method using the Agilent 5973N MSD.

Experimental

3-MCPD liquid (Sigma Scientific, St. Louis, MO.) was diluted in dichloromethane (VWR Scientific, San Francisco, CA). An aliquot was added to a reaction vial containing 1 mL isooctane and derivatized with heptafluorobutyrylimidazole (Pierce, Rockford, IL) at 70 °C for 30 minutes according to the procedure outlined in the AOAC method [2].

Results and Discussion

Derivatizing 3-MCPD with heptafluorobutyrylimidazole replaces the hydrogens on the diol groups with ester linkages to a perfluorinated propyl side chain. The molecular formula of the derivative is $C_3H_5O_2Cl(COC_3F_7)_2$, and Figure 1 shows the molecular structure. Figure 2 shows the electron impact (EI) ionization mass spectrum of the heptafluorobutyrylimidazole derivative of 3-MCPD from 60 to 510 *m/z*.

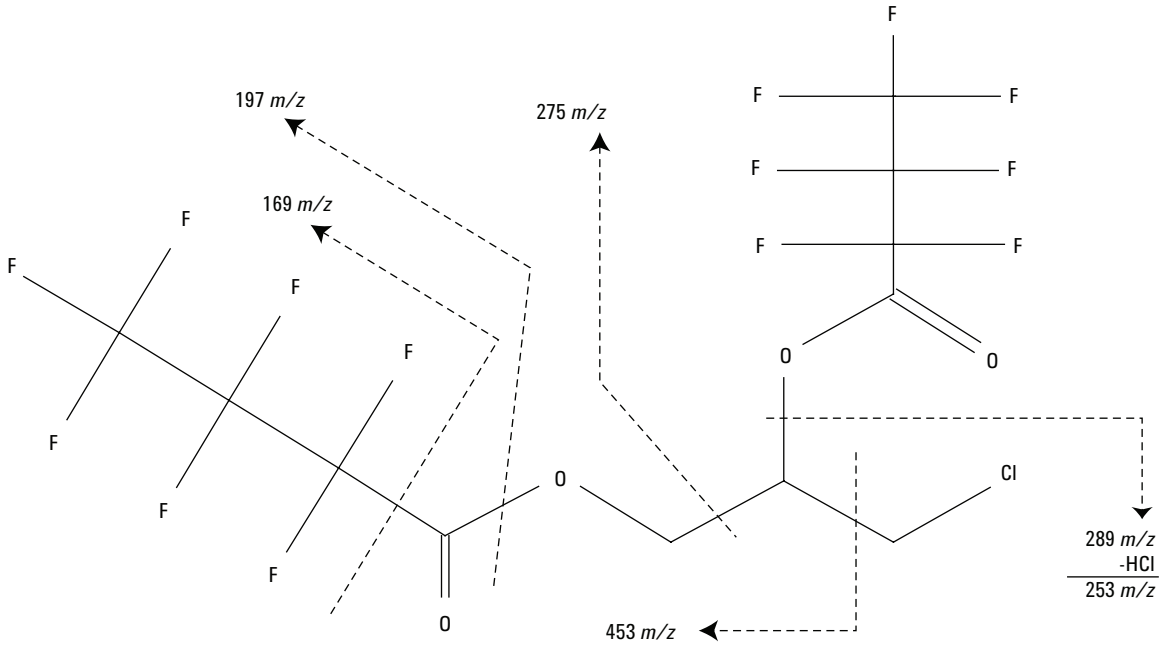


Figure 1. The molecular structure and a suggested fragmentation pattern for heptafluorobutyrylimidazole derivative of 3-MCPD in electron impact ionization.

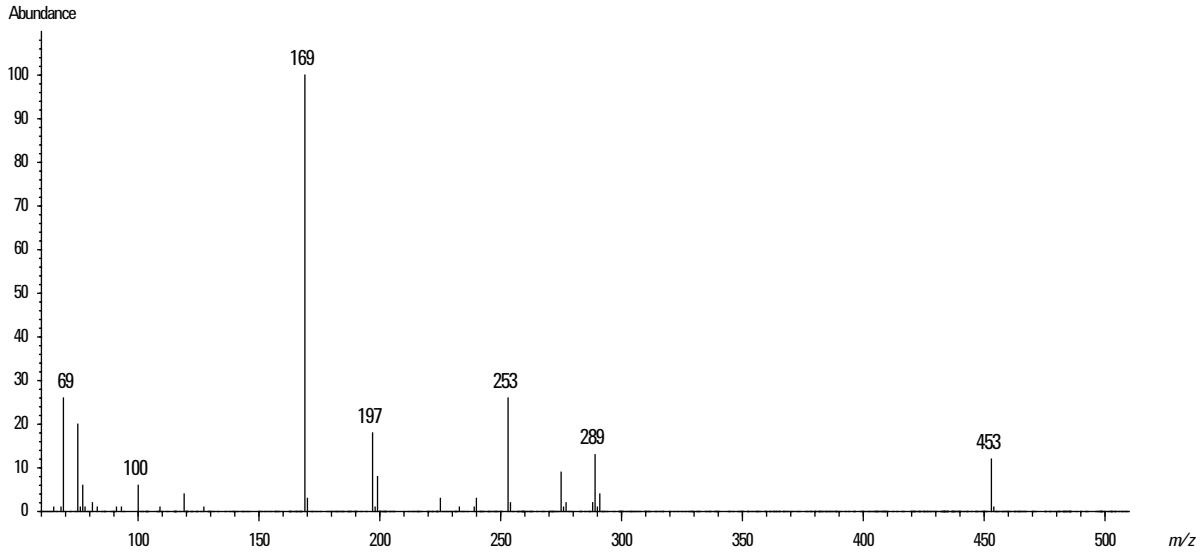


Figure 2. Electron impact ionization mass spectrum of the 3-MCPD heptafluorobutyryl derivative at 70 eV for the 60 to 510 *m/z* mass range. The molecular ion $[M]^+$ would be expected at 502 *m/z*.

Electron impact ionization produces a mass spectrum that lacks a molecular ion and has a base peak at *m/z* 169 from $[C_3F_7]^+$ fragments. As seen from the fragmentation diagram of Figure 1, the ions at 169 *m/z* and 197 *m/z* contain no structural relevance to 3-MCPD and consequently can not be used to indicate 3-MCPD. This suggests the 453, 289, 275, and 253 *m/z* fragments, which contain 3-MCPD structure, be used for detection. In the AOAC collaborative study, several laboratories had difficultly detecting the 453 *m/z* fragment. This is not a problem for the 5973N due to the high-energy dynode arrangement and high transmission quadrupole which provide good signal for high molecular weight fragments. In fact, work with the standard showed good signal-to-noise for the 453 *m/z* ion in the scan mode even at only a few picograms injected. Selected ion monitoring using the four ions suggests detection at subpicogram levels is possible.

In actual samples, matrix interferences may emerge and contribute to noise. However, the derivatization technique suggests applying electron capture negative ionization (ECNI) mass spectrometry which provides more selective ionization than electron impact. Figure 3 shows the ECNI mass spectrum of the 3-MCPD derivative under standard conditions with methane buffer gas (tat is, source 150 °C, methane at 2 mL/min). Unlike the EI results, the molecular ion (502 *m/z*) is detected, although at low relative intensity. Unfortunately like EI, the base peak at 213 m/z and next most abundant peak at 194 *m/z*, due to $[OCOC_3F_7]^+$ and $[OCOC_2F_7]^+$ fragments respectively, also contain no structural relationship to 3-MCPD. This leaves the 502, 482 and 446 *m/z* ions as good candidates for 3-MCPD detection and quantitation. Analysis of standards suggests that it would be possible to detect a few picograms in the scanning mode and less than one picogram in selected ion mode (SIM). Further optimization of ECNI is possible, such as a lower source temperature to take advantage of the low boiling point of the derivative, which may improve the spectrum and detection limits. The real advantage of ECNI is expected to be in typical food samples where the greater selectivity of ECNI will demonstrate a strong suppression of chemical noise and enhance method detection limits.

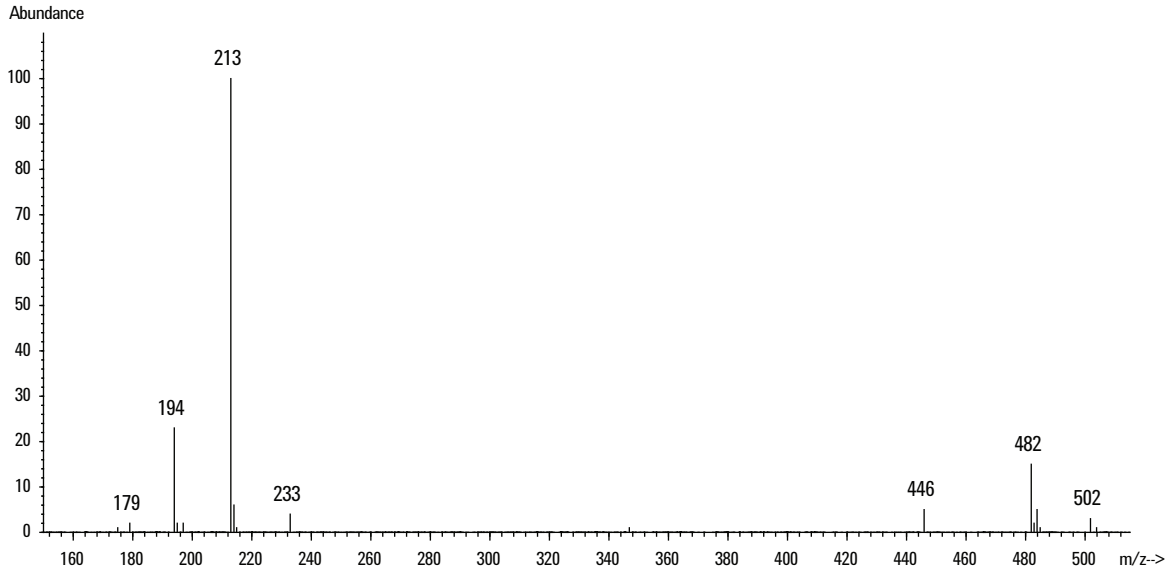


Figure 3. Electron capture negative ion chemical ionization mass spectrum of derivatized 3-MCPD with methane buffer gas from 150 to 510 *m/z*. Note the presence of the molecular anion $[M]^-$ not seen in EI.

Acknowledgments

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References

1. Reports of the Scientific Committee for Food, Food Sciences and Techniques, 36th Series, European Commission, Luxembourg, Belgium.
2. Brereton, P., et al., Determination of 3-chloro-1,2-propanediol in foods and food ingredients by gas chromatography with mass spectrometric detection: Collaborative study. *Journal of the AOAC International,* 2001. 84(2): p. 455-465.

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