Trends in Analytical Chemistry 62 (2014) 173–183

Contents lists available at ScienceDirect

Trends in Analytical Chemistry

journal homepage: www.elsevier.com/locate/trac

Application of modern sample preparation techniques to the determination of chloropropanols in food samples

Renata Jędrkiewicz *, Agnieszka Głowacz, Magdalena Kupska, Justyna Gromadzka, Jacek Namieśnik

Department of Analytical Chemistry, Faculty of Chemistry, Gdańsk University of Technology, 11/12 Narutowicza Str., Gdańsk 80-233, Poland

ARTICLE INFO

Keywords:
Chloropropanol
Derivatization
Determination
Dispersive liquid-liquid microextraction (DLLME)
Food contaminant
Food sample
Magnetic solid-phase extraction (MSPE)
Pressurized liquid extraction (PLE)
Sample preparation
Solid-phase microextraction (SPME)

ABSTRACT

Chloropropanols are heat-induced food toxicants that recently caused concern among industrial and scientific experts. World and European organizations related to food safety asked researchers to investigate mitigation strategies regarding these contaminants. The essential objective of this project was development of fast analytical methods enabling reliable determination and quantification of 3-monochloropropane-1,2-diol, 2-monochloropropane-1,3-diol and 1,3-dichloropropanol. There are now several widely applied methods, which meet the requirements to some extent, but they involve a multi-step sample-preparation process, rather undesirable in routine analysis. The solution seems to be application of modern extraction techniques, especially combined with derivatization, which may lead to shortening and simplifying the whole procedure.

We present the advantages of possible options for determination of chloropropanols by summarizing methods already developed involving techniques such as solid-phase microextraction, magnetic solid-phase extraction, pressurized liquid extraction or dispersive liquid-liquid microextraction.

Contents

Abbreviations: 1,3-DCP, 1,3-dichloropropanol; 2-MCPD, 2-monochloropropane-1,3-diol; 3-MCPD, 3-monochloropropane-1,2-diol; ACN, Acetonitrile; ASE, Accelerated solvent extraction; BSTFA, N,O-bis(trismethylsilyl)trifluoroacetamide; DI, Direct immersion; DLLME, Dispersive liquid-liquid microextraction; DVB/CAR/PDMS, Divinylbenzene/Carbowax/polydimethylsiloxane; EI, Electron ionization; HFBA, Heptafluorobutyric anhydride; HFBI, Heptafluorobutyrylimidazole; HS, Headspace; HVP, Hydrolyzed vegetable protein; LOD, Limit of detection; LPME, Liquid-phase microextraction; LVI, Large-volume injection; MSPE, Magnetic solid-phase extraction; MSTFA, N-methyl-N-(trimethylsilyl)trifluoroacetamide; NCI, Negative chemical ionization; OTT, Open tubular trapping; PA, Polyacrylate; PBA, Phenylboronic acid; PDMS, Polydimethylsiloxane; PFE, Pressurized fluid extraction; PLE, Pressurized liquid extraction; SPE, Solid-phase extraction; TDI, Tolerable daily intake; TMSI, Trimethylsilyl iodide.

* Corresponding author. Tel.: +48 58 347 21 28.
E-mail address: rjedrkiewicz@gmail.com (R. Jędrkiewicz).

http://dx.doi.org/10.1016/j.trac.2014.07.012
0165-9936/

1. Introduction

Known for decades, chloropropanols are a group of heat-induced food contaminants, which regained global attention quite recently. It is represented by three compounds well-described in the literature: 3-monochloropropane-1,2-diol (3-MCPD); 2-monochloropropane-1,3-diol (2-MCPD); and, 1,3-dichloropropanol (1,3-DCP) (Fig. 1).

Their presence in foodstuffs was reported in 1978 [in hydrolyzed vegetable protein (HVP) used for soy sauce production] [1], but the current renewed interest regarding this group relates to the high concentrations of their free and bound (esterified) forms reported recently in various foodstuffs, including thermally-treated foods, edible oils and fats and baby foods [2–5].

Chloropropanols and their esters are mainly formed in the presence of acylglycerols and chloride ions (Fig. 2) during thermal processing of fatty foodstuffs [e.g., refining of edible oils (particularly deodorization) and frying of carbohydrate-rich products] [6–8], but there are some who claim that the migration of chloropropanols from food packaging into foods and beverages is also possible [9]. The toxicity of these compounds is still under evaluation, especially because there are no toxicological data available regarding free and bound 2-MCPD and no European regulations concerning its occurrence in foods. 3-MCPD exhibits short-term and long-term toxicity, causing carcinogenic lesions on kidneys and testes, according to studies on rodents [10]. Mutagenic activity *in vitro* was observed, but studies *in vivo* did not prove this effect. The results of clinical studies on human beings have not been reported so far [11].

In 2001, on the basis of available toxicological data, experts of the Joint FAO/WHO Expert Committee on Food Additives (JECFA) and the EC Scientific Committee on Food established a maximum tolerable daily intake (TDI) for 3-MCPD of 2 μg/kg body weight per day and the regulatory limit of 0.02 mg/kg in foodstuff for HVP and soy sauce [12,13]. The main toxicological concern relates to the release of free 3-MCPD from its esterified form during digestion [14], as its overall quantity in human body may be critical. This process has not been fully described so far; that is why the risk assessment is based on the 100% release assumption.

Regarding 1,3-DCP, experts of the UK Committee on Carcinogenicity of Chemicals in Food, Consumer Products and the Environment and Committee on Mutagenicity of Chemicals in Food, Consumer Products and the Environment agreed that its genotoxicity and carcinogenicity *in vivo* may be prudentially assumed, and set the objective of reducing its concentration in foodstuffs to as low as technologically possible [15,16].

Because the problem of chloropropanols in foods appears to be a risk for human health and there are still not enough data or sometimes conflicting data exist, so preventing reliable assessment of this topic, scientists from industrial and academic field joined their investigations in order to fill the gaps in knowledge regarding chloropropanols. Undoubtedly, to reach this goal, there is a need for simple, fast analytical methods enabling determination of chloropropanols in food samples to develop a full toxicological profile and mitigation strategies.

The aim of this work is to draw attention to the possibility of applying modern sample preparation techniques in determination of chloropropanols in food samples. This article presents the main advantages of published methods applying techniques such

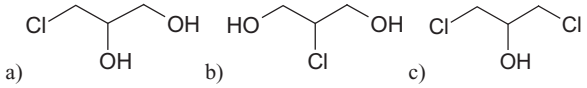

Fig. 1. Chemical structures of: a) 3-MCPD; b) 2-MCPD; and, c) 1,3-DCP.

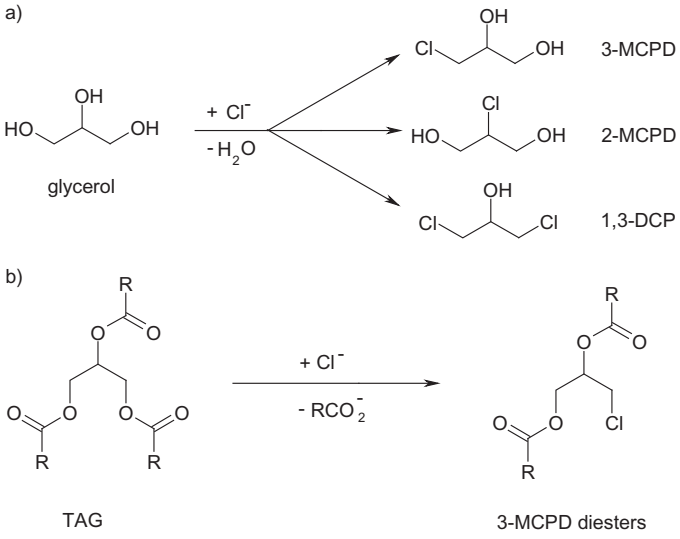

Fig. 2. The reaction scheme of formation of free and bound chloropropanols.

as solid-phase microextraction (SPME), magnetic solid-phase extraction (MSPE), accelerated solvent extraction (ASE) or dispersive liquid-liquid microextraction (DLLME), which, combined with derivatization, become powerful tools for the aim of fast, simple and environmentally friendly determination of 3-MCPD, 2-MCPD and 1,3-DCP, allowing low-limit detections, repeatability and reproducibility. These new procedures, which fulfill, to some extent, the requirements of the concept of sustainable development expressed by green chemistry and green analytical chemistry, may be a reasonable alternative for currently widely-applied and recommended methods with a multi-step sample-preparation process involving the use of many chemicals. This summary of the application of modern analytical techniques in determination of chloropropanols in food samples brings novelty to both analytical chemistry and food chemistry.

2. Derivatization as a key step

A derivatization reaction is applied before GC analysis in order to improve the volatility of target analytes and, as a result, to improve peak symmetry, resolution, selectivity and sensitivity of the analytical method [17]. General factors that an appropriate derivatization agent should provide are:

1 formation of a characteristic derivative for each compound;
2 rapid reaction carried out under mild, easy-to-obtain conditions;
3 high and repeatable yield of derivative; and,
4 stability of the derivative in the reaction medium [18].

The efficiency of a derivatization reaction is often affected by such factors as matrix complexity, temperature, agitation, additional enhancement (ultrasound and microwaves), pH, amount and concentration of the derivatization agent, and type of solvent used [19].

Low volatility and high polarity of chloropropanols make their determination by GC practically impossible without derivatization reaction. The initial methods of underivatized 3-MCPD determination resulted in low sensitivity, poor peak shape (peak broadening) and interfering unfavorable reactions, which caused them to be excluded because of non-compliance with European regulations [20]. There were some efforts to apply the headspace (HS) technique for underivatized 1,3-DCP determination and the method appeared to be rapid and sensitive enough [21], but its main disadvantage was the inability determine 3-MCPD and 1,3-DCP simultaneously [22].