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Quantitative analysis of aldehydes in canned vegetables using static headspace–gas chromatography–mass spectrometry

María Serrano, Mercedes Gallego*, Manuel Silva

Department of Analytical Chemistry, Campus of Rabanales, University of Córdoba, E-14071 Córdoba, Spain

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ABSTRACT

Volatile aldehydes appear in canned vegetables as constituents and some of them can also be present as disinfection by-products (DBPs) because of the contact between vegetables and treated water. This paper describes two static headspace–gas chromatography–mass spectrometry (SHS–GC–MS) methods to determine 15 aldehydes in both the solid and the liquid phases of canned vegetables. The treatment for both phases of samples was carried out simultaneously into an SHS unit, including the leaching of the aldehydes (from the vegetable), their derivatization and volatilization of the oximes formed. Detection limits were obtained within the range of 15–400 μg/kg and 3–40 μg/L for aldehydes in the solid and the liquid phases of the food, respectively. The relative standard deviation was lower than 7% –for the whole array of the target analytes–, the trueness evaluated by recovery experiments provided %recoveries between 89 and 99% and short- and long-term stability studies indicated there was no significant variation in relative peak areas of all aldehydes in both phases of canned vegetables after their storing at 4 °C for two weeks. The study of the origin of the 15 aldehydes detected between both phases of canned vegetables showed that: i) the presence of 13 aldehydes –at average concentrations of 2.2–39 μg/kg and 0.25–71 μg/L for the solid and the liquid phases, respectively– is because they are natural constituents of vegetables; and ii) the presence of glyoxal and methylglyoxal –which are mainly found in the liquid phase (average values, 1.4–4.1 μg/L)– is ascribed to the use of treated water, thereby being DBPs.

1. Introduction

Canned vegetables make up a significant fraction of the total vegetable consumption [1]. Vegetables are rich in polyphenolic compounds such as flavonoids, which can react with amino acids, carbohydrates, and lipids to produce volatile flavor compounds, including aldehydes. The Strecker degradation of amino acids –leading to structurally related flavorful aldehydes– is a widely known and well-investigated reaction [2]. Many Strecker aldehydes are important flavor substances, *e.g.* methional, acetaldehyde (C2), 2-methylpropanal (2-MP), 2-methylbutanal (2-MB) and 3-methylbutanal (3-MB) [3]. Other low-molecular mass aldehydes, like formaldehyde (C1) and C2 are naturally present as a product of normal metabolism in many foods including fruits and vegetables [4]. Other volatile aldehydes, such as hexanal (C6) and nonanal (C9), are the main contributors to the characteristic odor of plants, being produced by the lipoxygenase pathway and involved in wound healing and pest resistance. Thus, C6 and C9 have been widely used as food flavors to reconstitute the "fresh green" odor lost during vegetable processing [5]. Among aldehydes, C1 and C2 have been the most frequently determined in food [4]. C1 has been found at high concentrations between 2.5 and 26.2 mg/kg in cereals, fish, vegetables, fruits and milk because it can be fraudulently added as formalin in Asian countries [6]. Concentrations of C2 found in canned and fresh vegetables were 0.1–4.5 and 0.1–5.6 mg/kg, respectively [7]. Other aldehydes such as butanal (C4), 2-MP, 2-MB, 3-MB, pentanal (C5), C6, heptanal (C7), octanal (C8) and C9 are commonly known as flavor components of the carrot juice [8] and kidney beans [9].

C1 and C2 are recognized genotoxicants, being their toxicities related to their ability to undergo 1,2-addition reactions with amines [10]. Nonetheless, no legislation has been reported for the control of these aldehydes in food so far; only the World Health Organization has established a health-based guideline concentration of 900 μg/L for C1 in drinking water [11]. Other volatile aldehydes –such as glyoxal (G) and methylglyoxal (MG) – seem to form adducts or modify DNA, resulting in mutagenicity, the last being 10-fold more effective than G at crosslinking DNA [12].

Despite toxic effects and volatility of aldehydes, few methods have been reported for their determination in food, probably due

* Corresponding author.
E-mail address: mercedes.gallego@uco.es (M. Gallego).

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to the complexity of the matrix. In fact, the literature has been focused on C1, C2 and C6 aldehydes due to the fact they are important constituents of the characteristic flavor of fruits, vegetables and green leaves [6,7,13–15]. Another consequence of the high volatility of aldehydes, in addition to their reactivity and polarity, is the complication of their direct analysis. As a result, the derivatization of aldehydes –especially those with low-molecular mass– prior to their analyses is mandatory. O-2,3,4,5,6 (pentafluorobenzyl) hydroxylamine and 2,4-dinitrophenylhydrazine (DNPH) are typical reagents for the derivatization of aldehydes with gas chromatography (GC) and liquid chromatography (LC) analysis, respectively. LC has been occasionally employed to determine C1 in fruits and vegetables after derivatization with DNPH and detection by DAD (λ = 355 nm) [6]. The same technique has been applied for the determination of 12 aldehydes in cooked food by LC–mass spectrometry (MS) [16]. In this method, the sample treatment included both the derivatization with DNPH and a clean-up step by solid phase extraction. According to the volatility of the aldehydes, GC has been the most used technique for their determination. The most simplistic method for C2 determination in vegetables included headspace (HS)–GC–Flame ionization detector without derivatization, providing a limit of quantification (LOQ) of 0.1 mg/kg [7]. It is a fact that the concentrations of C6 aldehydes in tomato are important factors related to the flavor quality of the food [13,14]. For this reason, C6 aldehydes have been determined in tomato by thermal desorption–GC–MS [13] or by solid phase microextraction/GC–MS with LOQ of 6.7 ng/L [14]. In addition, up to 10 aldehydes have been found as odor constituents of carrot juices using Purge and Trap–GC–MS for qualitative analyses [8]. The sample treatment of the above referenced methods needs high solvent consumption, centrifugation or filtration [6,16], and they are time consuming (25–60 min).

It is important to note that chlorine-based sanitizers are the most commonly used disinfectants in food processing plants, producing carcinogen disinfection by-products (DBPs) through the reaction between sanitizers and food components (carbohydrates, lipids, etc.), among other pathways [17]. In fact, noticeable concentrations of trihalomethanes and haloacetic acids have been recently found in dairy products [18,19], and canned vegetables [20]. In the case of aldehydes –identified as DBPs after water treatment with chlorine-containing disinfectants–, C1–C5, benzaldehyde (BA), G and MG have been determined –at concentrations between 0.1 and 5.1 μg/L in treated water– using an SHS–GC–MS method [21]. More recently, propanal (C3), C4, C5, BA, G and MG have been also found as DBPs in reconstituted juices, nectars and soft drinks at concentrations related with the amount of treated water used as ingredient in these beverages [22].

Based on the foregoing, it can be concluded that volatile aldehydes can be found in canned vegetables as constituents of the characteristic flavor of green leaves and vegetables and/or as DBPs because of the contact between vegetables and treated water. Therefore, DBPs can appear in vegetables through several routes, namely: i) washing the vegetable with treated water, ii) disinfection of food-processing equipment, and iii) using treated water in the preparation of vegetables (scalding process and/or heat treatment with brine solutions or sauces). Hence, in order to perform the present research, 15 representative aldehydes that can be naturally present in vegetables have been selected (C1–C9, 2-MP, 2-MB, 3-MB and BA) or as DBPs (C1–C5, BA, G and MG). Due to the origin (natural/DBPs) and polarity of the target aldehydes, they can be found in both the solid (edible) and the liquid (non-edible) phases –which can be ingested to some extent–, of canned vegetables. Therefore, the monitoring of aldehyde concentrations in both the solid and the liquid phases of canned vegetables could be an interesting study. Taking into account that the SHS technique is suitable for the analysis of volatile compounds in solid matrices, the aim of the present work was the development of two SHS–GC–MS methods for the determination of 15 aldehydes in the solid and liquid phases of canned vegetables.

2. Materials and methods

2.1. Chemicals and standards

Formaldehyde (37% w/v solution in water), acetaldehyde (99.5%), 2-methylpropanal (99%), 2-methylbutanal (95%), 3-methylbutanal (97%), hexanal (98%), heptanal (95%), octanal (95%), nonanal (99%), benzaldehyde (99%), methylglyoxal (40% solution in water), *o*-2,3,4,5,6-pentafluorobenzyl hydroxylamine hydrochloride (PFBHA, 98%) and the internal standard (IS, 1,2-dibromopropane) were purchased from Sigma-Aldrich (Madrid, Spain). Analytical grade of propanal, butanal and pentanal and glyoxal (40% solution in water) was supplied by Fluka (Madrid, Spain). Other reagents were of analytical grade. Individual stock standard (1 g/L) and dilute combined (50 μg/mL) solutions were prepared in methanol and stored in amber glass vials at −20 °C. Ultra-grade water (Sigma-Aldrich) free of aldehydes was used to prepare aqueous solutions for fortification purposes.

2.2. Chromatographic conditions

Analyses were carried out on an HP 7890A gas chromatograph-5975C mass selective detector equipped with a G1888 static headspace autosampler (Agilent Technologies, Palo Alto, CA). The operating conditions for the SHS autosampler were as follows: vial equilibration time, 20 min; oven temperature, 80 °C; vial pressurization time, 30 s; loop fill time, 9 s; transfer line temperature, 110 °C. Helium was used both to pressurize the vial and to transfer the loop content (3 mL) to the injection port of the gas chromatograph, which was equipped with an HP-5MS [(5%)-phenyl-(95%)-methylpolysiloxane] fused silica capillary column (30 m × 0.25 mm, 0.25 μm film thickness) supplied by Agilent. Sample injection was done in split mode (1:20 split ratio) for 1 min with an inlet temperature of 250 °C (1 mL/min helium flow-rate). The chromatographic oven temperature program was as follows: 40 °C, held for 4 min, 5 °C/min to 200 °C, then 20 °C/min to 250 °C and held for 1 min. A solvent delay of 7 min was fixed. The transfer line and ion source temperatures were maintained at 250 °C. Optimization was conducted in total ion chromatogram mode and quantification of the target aldehydes was performed in SIM mode using m/z 181 as the quantifying ion (highest intensity). Suitable fragments for identifying each aldehyde with a dwell time of 50 s as well as their acronyms and retention times (t_r) are listed in the table of the analytical characteristics of the method.

2.3. Samples

The whole array of the canned vegetables analyzed in this investigation was purchased at local markets in Spain. Vegetables were stored in their original packages (can and glass), unopened at room temperature until their analyses. After the package was opened, the solid and the liquid phases were separated by sifting. A portion of the solid phase (about 50 g) of canned vegetables was crushed and homogenized in an agate mortar. The liquid phase (about 50 mL) of canned vegetables was transferred to a glass bottle of 50 mL. In the case of canned vegetables preserved in vinegar, their liquid phases were adjusted to pH 8.0–9.0 with NaOH before analysis.

The optimization of the method was carried out by using pickles as representative model –since they did not contain significant amount of the aldehydes studied– of the whole array of commercially available canned vegetables. To study the ratio vegetable amount:extractant volume (w/v) and the pH of the liquid phase of

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